Hydrogen and Fuel Cells Program
2017 Annual Merit Review and Peer Evaluation Meeting
Washington, DC – June 5-9, 2017

ElectroCat (Electrocatalysis Consortium)

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Project ID: FC160

Overview

Timeline

- **Start date** (launch): Feb 1, 2016
- **End date:** Sep 30, 2020

Budget

- **FY16 funding:** $2,100K
- **FY17 funding:** $3,500K
- **Total FY16 - FY17:** $5,600K

Barriers

- **A. Cost** (catalyst)
- **D. Activity** (catalyst; MEA)
- **B. Durability** (catalyst; MEA)
- **C. Power density** (MEA)

Note: This is the first evaluation of ElectroCat at a DOE Annual Merit Review.

Partner – PI

Los Alamos National Laboratory – Piotr Zelenay

Argonne National Laboratory – Deborah Myers

National Renewable Energy Laboratory – Huyen Dinh

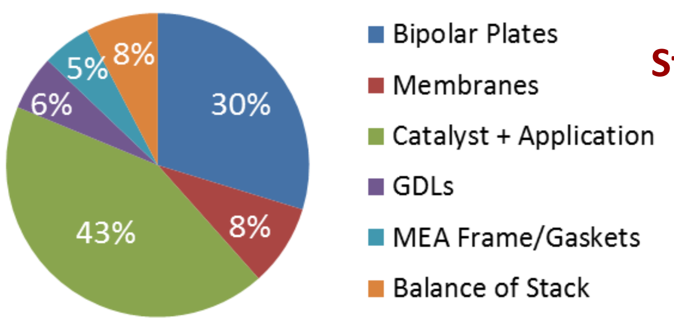
Oak Ridge National Laboratory – Karren More

Relevance: Fuel Cell Stack Cost Challenge

Fuel cell system targets set to be competitive with ICEVs

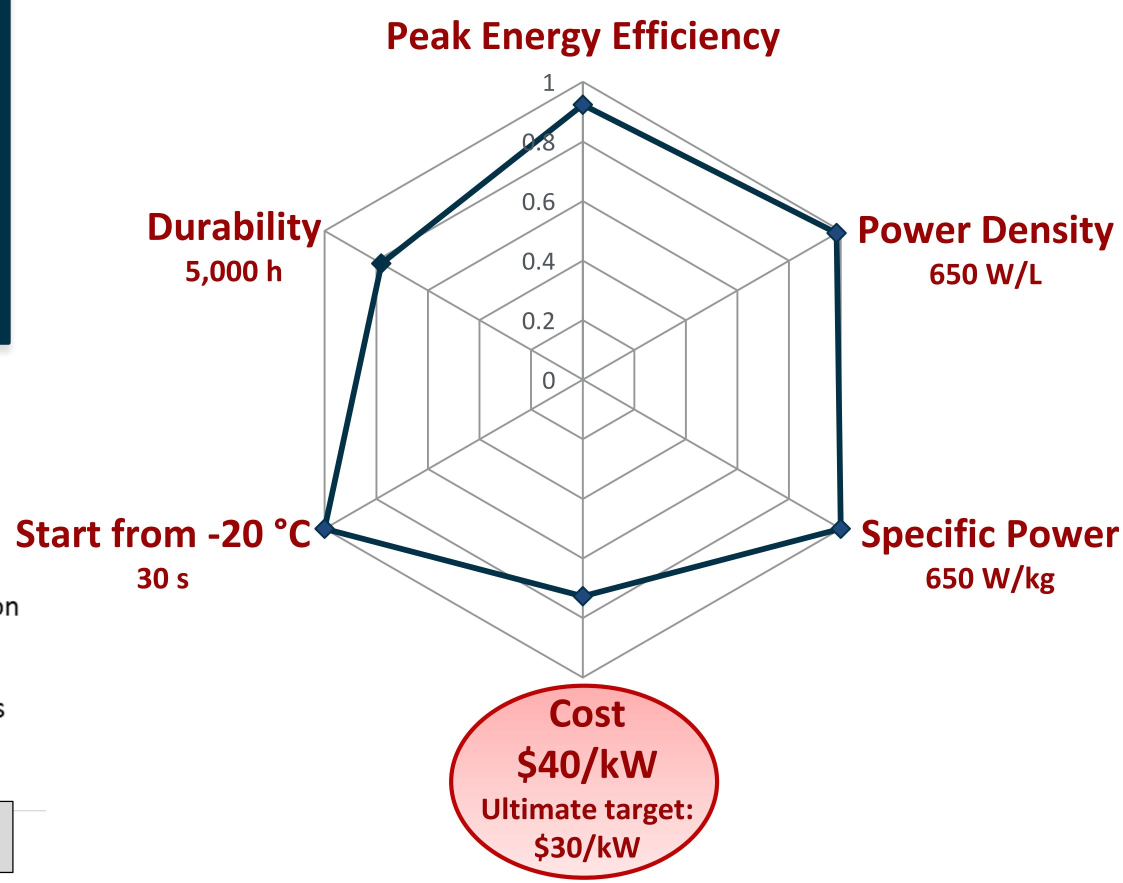
Durability and cost are the primary challenges to fuel cell commercialization and must be met concurrently

PGM Stack Cost Breakdown
(500,000 systems/year)



https://www.hydrogen.energy.gov/pdfs/16020_fuel_cell_system_cost_2016.pdf

PGM-based System Automotive Stack Status



ElectroCat created as part of Energy Materials Network in February 2016
U.S. Department of Energy

Goal: Accelerate the deployment of fuel cell systems by eliminating the use of PGM catalysts

Approach: ElectroCat Objectives and Lab Roles

Mission: Develop and implement PGM-free catalysts and electrodes by streamlining access to unique synthesis and characterization tools across national labs, developing missing strategic capabilities, curating a public database of information.

Materials Discovery and Development	**Catalysts** for oxygen reduction in low-temperature PEFCs and PAFCs
	Catalysts for oxygen reduction and hydrogen oxidation in AMFCs
	Development of **electrodes** and **MEAs** compatible with PGM-free catalysts
Tool Development	Optimization of **atomic-scale** and **mesoscale models** of catalyst activity to predict macro-scale behavior
	High-throughput techniques for catalyst synthesis
	High-throughput techniques for characterization of catalysts, electrodes, and MEAs
	Aggregation of data in an easily searchable, public database to facilitate the development of catalyst materials and MEAs

Los Alamos National Laboratory
Argonne National Laboratory
NREL National Renewable Energy Laboratory
Oak Ridge National Laboratory

LANL: PGM-free catalyst development, electrochemical and fuel cell testing, atomic-scale modeling
ANL: High-throughput techniques, mesoscale models, X-ray studies, aqueous stability studies
NREL: Catalyst modification, model catalyst development, advanced fuel cell characterization
ORNL: Advanced electron microscopy, atomic-level characterization, XPS studies

Approach: Performance Targets

Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications			
Characteristic	**Units**	**2015 Status**	**2020 Targets**
Platinum group metal total content (both electrodes)	g / kW (rated, gross) @ 150 kPa (abs)	0.16	0.125
Platinum group metal (pgm) total loading (both electrodes)	mg PGM / cm^2 electrode area	0.13	0.125
Mass activity	A / mg PGM @ 900 $mV_{iR\text{-}free}$	>0.5	0.44
Loss in initial catalytic activity	% mass activity loss	66	<40
Loss in performance at 0.8 A/cm^2	mV	13	<30
Electro catalyst support stability	% mass activity loss	41	<40
Loss in performance at 1.5 A/cm^2	mV	65	<30
PGM-free catalyst activity	A / cm^2 @ 900 $mV_{IR\text{-}free}$	0.016	>0.044

Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan - Section 4.4 Fuel Cells, DOE 2016

PGM-free activity target equivalent to PGM activity target:

$0.44\ A/mg_{PGM} \times 0.1\ mg_{PGM}/cm^2_{(electrode\ area)} \rightarrow$ **$0.044\ A/cm^2$**

Approach: FY16 Milestone, FY17 LANL and ANL QPMs

FY16

Date	ElectroCat Annual Milestone	Status
September 2016 (FY16 Q4)	Establish a web-based Portal for the Consortium through which industry and university partners can easily and quickly identify the Consortium tools that would be most useful to them.	**Completed** (see Slide 9)

FY17

Date	LANL Quarterly Progress Measures	Status
December 2016 (FY17 Q1)	Develop draft TT/A plan for ElectroCat and receive feedback from member national laboratories.	**Completed** (see Slide 11)
March 2017 (FY17 Q2)	Synthesize and, in collaboration with other ElectroCat partner laboratories, characterize and evaluate ORR activity of PGM-free catalysts based on di-iron complexes.	**Completed** (see Slide 41, Back-up)
June 2017 (FY17 Q3)	Synthesize and demonstrate atomic dispersion of Fe sites in (Zn, Fe)-PSIE-MOF-derived catalyst; provide samples to ANL for further development of high-throughput screening techniques.	**On track**

Date	ANL Quarterly Progress Measures	Status
December 2016 (FY17 Q1)	Achieve half-wave potential agreement of <20 mV between RDE and m-CFDE ORR measurements for a benchmark PGM-free catalyst.	**Completed** (with $E_{½}$ agreement of < 30 mV)
March 2017 (FY17 Q2)	Select and prepare six PGM-free electrode specimens and obtain 3-D micro-structures using synchrotron XCT.	**Completed** (for 7 ADC electrodes)
June 2017 (FY17 Q3)	Demonstrate current densities in the combinatorial MEA for all twenty-five electrodes within 10% of those in a standard 5 cm² test cell using identical PGM-free electrode compositions in both cells.	**On track**

ElectroCat
Electrocatalysis Consortium

Approach: FY17 NREL QPMs

FY17

Date	NREL Quarterly Progress Measures	Status
December 2016 (FY17 Q1)	Demonstrate F-doping onto LANL's PGM-free catalyst (e.g., Fe-CM-PANI-C catalyst) with either CF_4 or F_2.	**Completed** (see Slide 46)
March 2017 (FY17 Q2)	Demonstrate the synthesis of the M-C-N model catalyst with the chemical composition comparable to state of the art literature, and study its structural properties. The first target moiety is a nitrogen coordinated transition metal center in a carbon matrix, e.g., FeN_4 in graphene matrix.	**Completed** (see Slide 28)
June 2017 (FY17 Q3)	Demonstrate improved feasibility of segmented cell system for combinatorial PGM-free samples (e.g., Fe-CM-PANI-C catalyst) to minimize cross-talk of a one electrode layer with gradient composition and allow for a sufficient resolution and data interpretation. Based on availability, demonstration performed either with standard (i.e., non-combinatorial) PGM-free samples or first generation combinatorial Pt or PGM-free samples	**On track**
September 2017 (FY17 Q4)	Extract values for the reaction order with respect to oxygen partial pressure and activation energy as a function of PGM-free catalyst type and/or electrode design. Utilize these extracted values to help determine the reaction mechanism for said PGM-free electrocatalyst (e.g., Fe-CM-PANI-C catalyst).	**On track**

Approach: FY17 ORNL QPMs, Milestone and Go/No-Go Decision

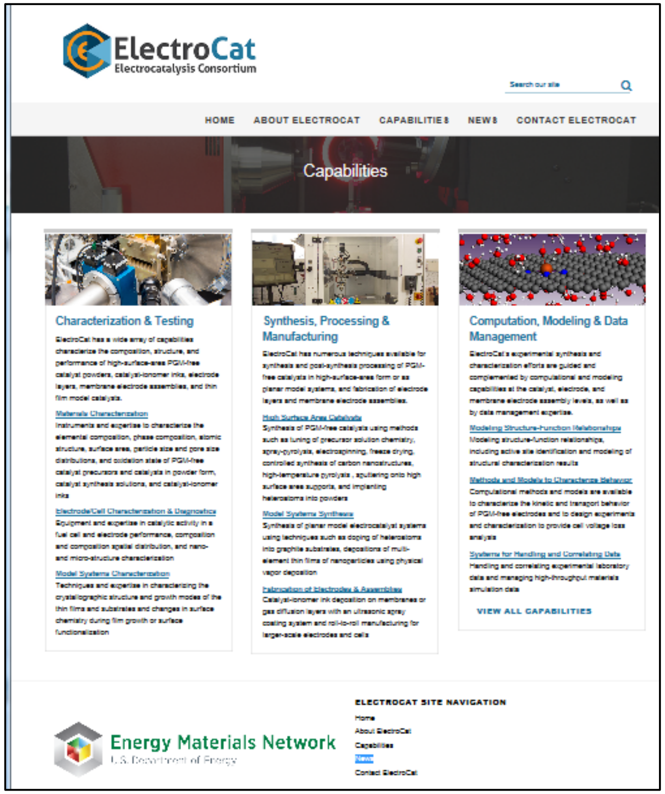
FY17

Date	ORNL Quarterly Progress Measures	Status
December 2016 (FY17 Q1)	Characterize at least three new candidate PGM-free catalysts using STEM imaging and analysis and XPS.	**Completed**
March 2017 (FY17 Q2)	Coordinate characterization effort at ORNL with high-throughput combinatorial results from ANL towards down-selecting potential catalysts for in-depth structural and chemical analyses.	**On track**
June 2017 (FY17 Q3)	Coordinate 3D electron tomography effort at ORNL with 3D X-ray tomography efforts from both ANL and LANL.	**On track**

Date	ElectroCat Annual Milestone	Status
September 2017 (FY17 Q4)	Demonstrate 20 mA cm^{-2} at 0.90 V (*iR*-corrected) in an H_2-O_2 fuel cell and 100 mA cm^{-2} at 0.80 V in an H_2-air fuel cell (measured); maintain partial pressure of O_2 + N_2 at 1.0 bar (cell temperature 80 °C).	**On track** (see Slide 13)

Date	ElectroCat Go/No-Go Decision	Criteria	Decision
June 2017 (FY17 Q3)	**TT/A Process:** Continuation of current path toward establishing a technology transfer and agreement (TT/A) process.	Short-form agreement for rapidly engaging industry established.	**TBD**

Accomplishment: Capabilities Posted on ElectroCat Website



Synthesis, Processing and Manufacturing

Synthesis and post-synthesis processing of PGM-free catalysts in high-surface-area form or as planar model systems, and fabrication of electrode layers and MEAs

- ✓ High surface area catalysts
- ✓ Model systems synthesis
- ✓ Fabrication of electrodes and membrane-electrode assemblies

Characterization and Testing

Composition, structure, and performance of high-surface-area PGM-free catalyst powders, catalyst-ionomer inks, electrode layers, membrane electrode assemblies, and thin film model catalysts.

- ✓ Materials Characterization
- ✓ Electrode/Cell Characterization & Diagnostics
- ✓ Model Systems Characterization

Computation, Modeling and Data Management

Guiding and complementing experimental efforts with computational and modeling capabilities at the catalyst, electrode, and membrane electrode assembly levels, as well as by data management expertise.

- ✓ Modeling structure-function relationships
- ✓ Methods and models to characterize behavior
- ✓ Systems for handling and correlating data

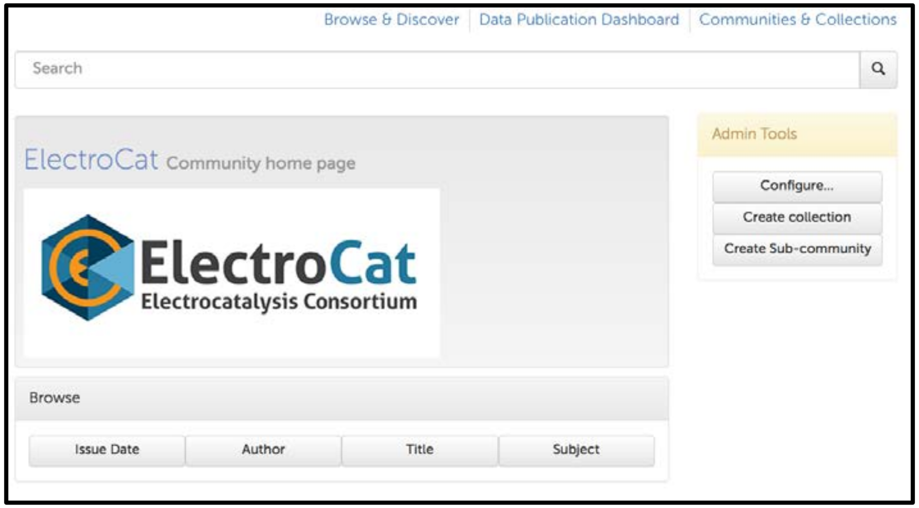
http://www.electrocat.org/capabilities/

Milestone: FY16 ElectroCat milestone completed (FY16 Q4)

Accomplishment: Data Hub Established

Prototype Data Hub for Internal Group
(available)

Web user interface (UI) for general access



Python and REST interfaces to support automation and scripting

1 Configure

```
import autopublish
config = {
    "source_ep" : "e38ee745-6d04-11e5-ba46-22000b92c6ec",
    "source_path" : "/MDF/testing_publication/data2/",
    "metadata_path": "/MDF/testing_publication/data2/data2_metadata.json"
}
```

2 Publish dataset

```
autopublish.publish(**config)
```

Data Hub Team Activities:

- Established monthly Data Team meetings with PIs to discuss ongoing data efforts
- Leveraging Globus data publication and Globus search services for prototype Data Hub

Data Hub features to be implemented:

- Capability to mint DOIs or other permanent identifiers with persistent landing pages for datasets
- Support for publishing datasets with sizes ranging from kB to TB
- Tools to support automated data capture and publication
- Capabilities to share datasets internally and externally

Accomplishment: Technology Transfer and Agreements (TT/A)

Non-Disclosure Agreement (NDA) → Information Disclosure

Intellectual Property Management Plan → IP Protection

Sponsored Research Agreements (CRADAs and SPPs) → Collaboration

Licensing and Material Transfer Agreements (MTAs)

↓

Access / Freedom to Operate

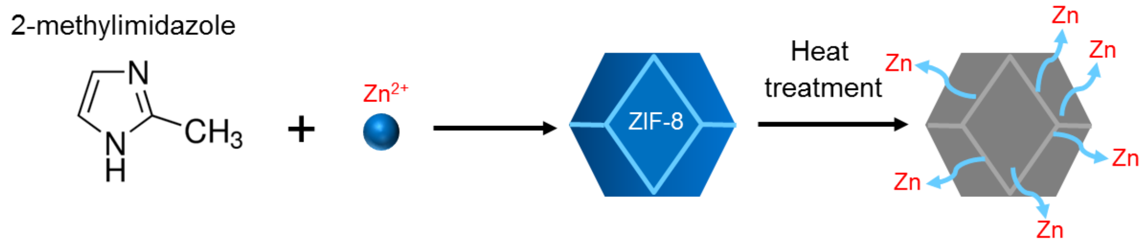
- **Industry Engagement Plan** (IEP) – finalized and agreed upon
- **Multi-Laboratory Non-Disclosure Agreement** (NDA) – executed

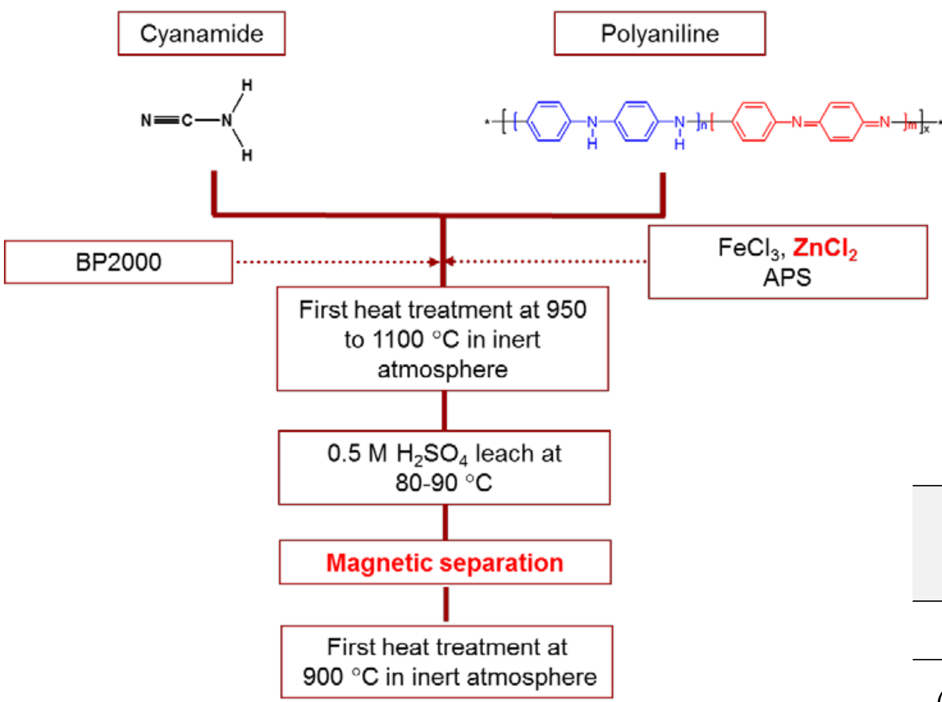
- **Intellectual Property Management Plan** (IPMP) – in process
- **Material Transfer Agreement** (MTA) – in process
- **CRADA Template** – complete; previously agreed upon format; available for use
- Tech Transfer and Agreements group conference call held in March 2017 to discuss TT/A strategy and status update

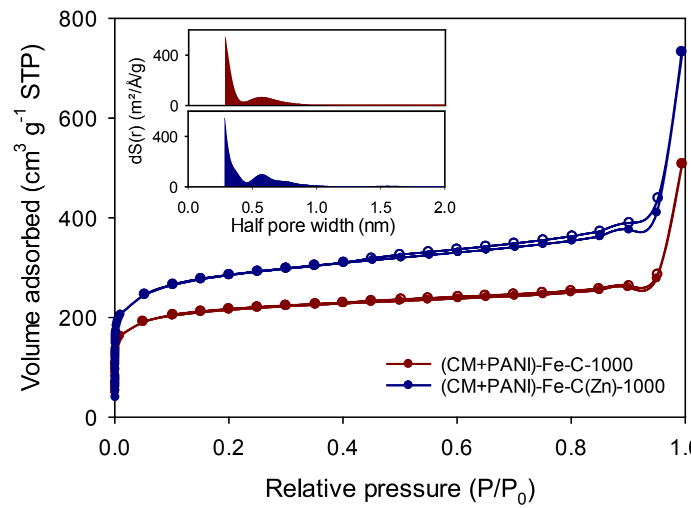
Highlight: FY17 Q1 Quarterly Progress Measure Completed

Progress: (CM+PANI)-Fe-C(Zn) Catalyst

Zn salt used instead of Zn-MOF to synthesize highly porous catalyst at temperatures above 900 °C



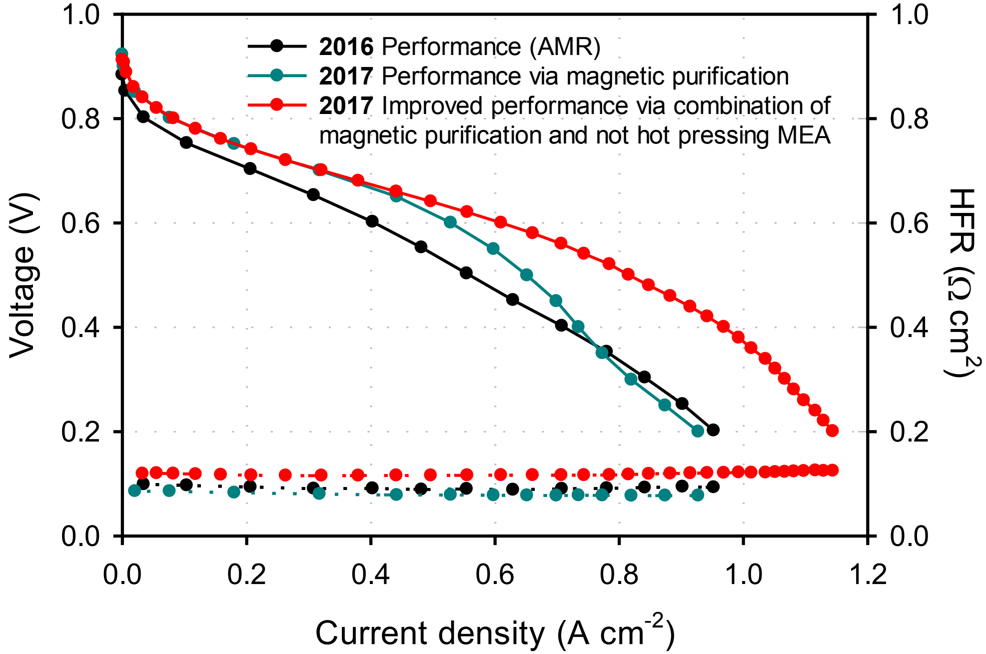


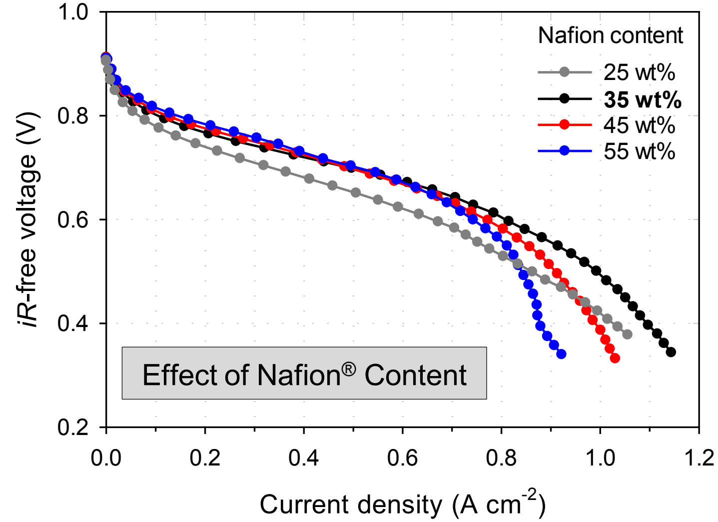


Sample	BET surface area ($m^2\ g^{-1}$)	Micropore surface area ($m^2\ g^{-1}$)
(CM+PANI)-Fe-C-1000	716	880
(CM+PANI)-Fe-C(Zn)-1000	1029	1086

Accomplishment: Fuel Cell Performance of (CM+PANI)-Fe-C(Zn) Catalyst

Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure;
Cathode: *ca.* 4.8 mg cm^{-2} air, 200 sccm, 1.0 bar air partial pressure;
Membrane: Nafion®,211; **Cell:** 5 cm^2, 80 °C





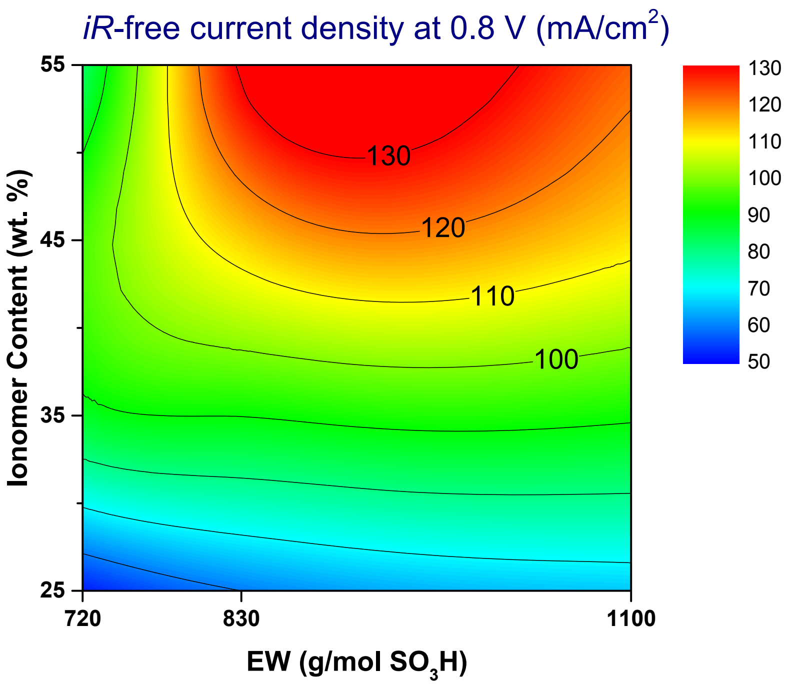
Ionomer content (wt. %)	25	35	45	55
iR-free current density at 0.8 V (mA cm^{-2})	65	90	110	120

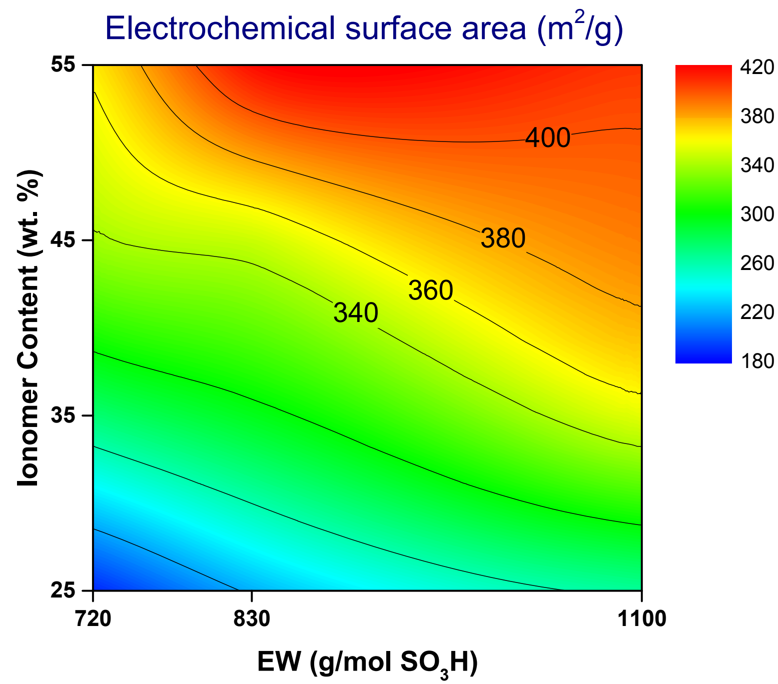
- Kinetic region improved by increasing micropore surface area by Zn evaporation and removing spectator magnetic Fe species (magnetic purification, see Slide 41)
- Mass transport region is further improved by removing hot pressing step

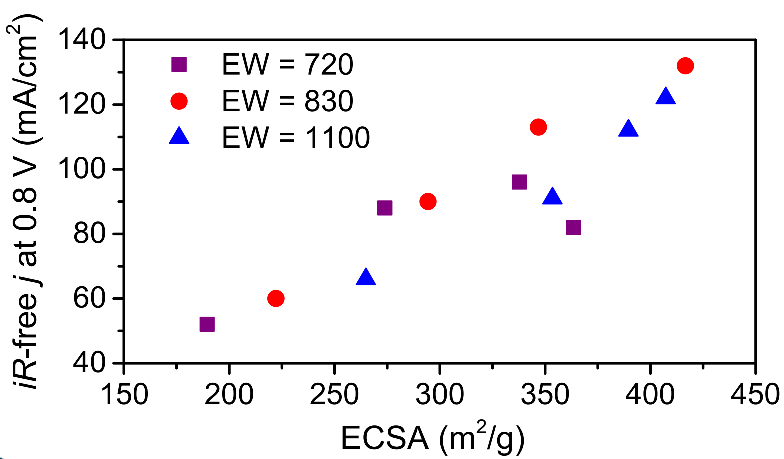
Highlight: Improved fuel cell performance in both kinetic and mass transport region reaching a current density of 120 mA/cm^2 at 0.8 V (*iR*-free)

Progress: Effect of Ionomer Content and Equivalent Weight (EW)

Anode: 0.3 $mg_{Pt}\,cm^{-2}$ Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** (CM+PANI)-Fe-C(Zn) *ca.* 4.8 mg cm^{-2} (not hot-pressed), air, 200 sccm, 1.0 bar air partial pressure; **Ionomers:** Nafion D521 (EW 1100), Aquivion D83 (EW 830), Aquivion D72 (EW 720); **Membrane:** Nafion® 211; **Cell:** 5 cm^2, 80 °C



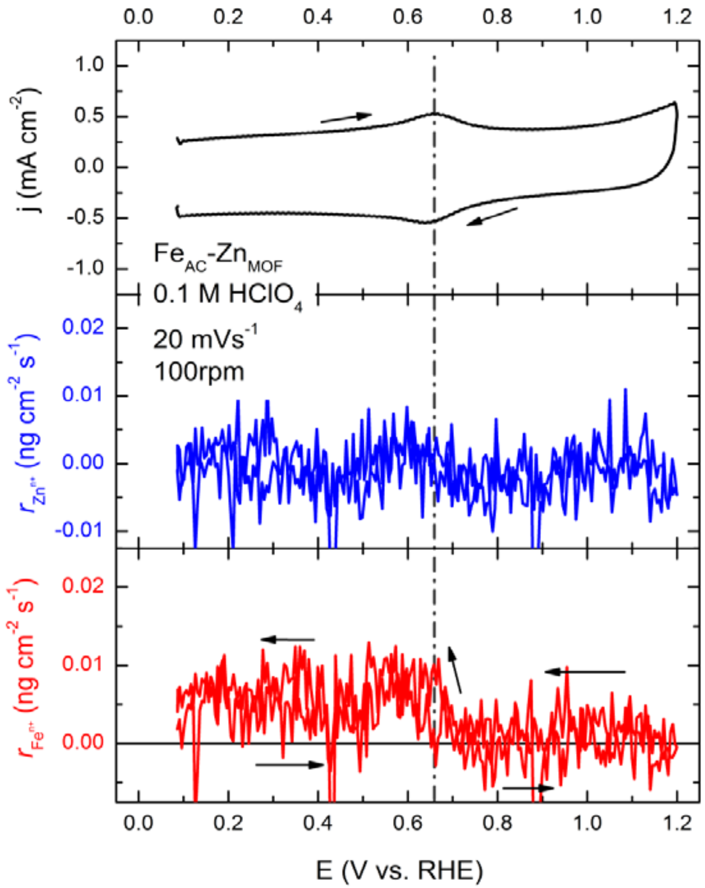




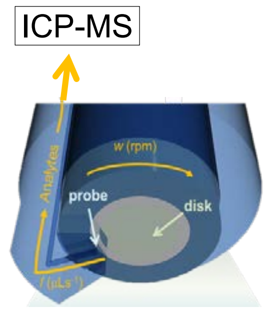
Increasing ionomer content from 25 wt% to 55 wt% improves kinetic performance thanks to higher catalyst utilization, *i.e.*, higher electrochemically-active surface area (ECSA)

Accomplishment: *In situ* RDE-ICP/MS of PGM-Free Catalysts

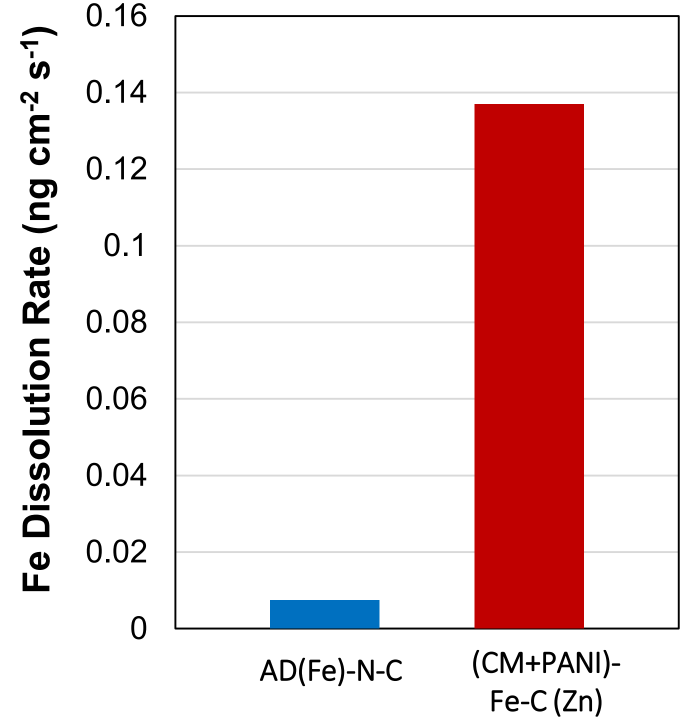
MOF-derived atomically dispersed **(AD)Fe-N-C** PGM-free catalyst



LANL (AD)Fe-N-C: 0.3 mg/cm^2; potential cycling range: 0.08 - 1.2 V vs. RHE; RDE at 100 rpm



~ 0.2 at% Fe in both (AD)Fe-N-C and (CM+PANI)-Fe-C(Zn)

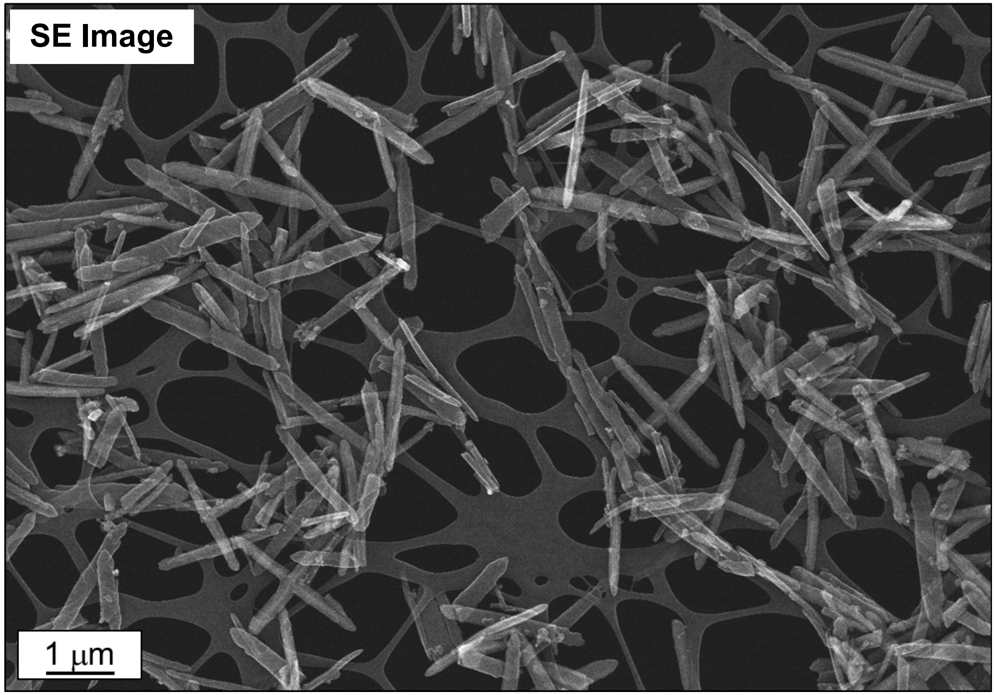


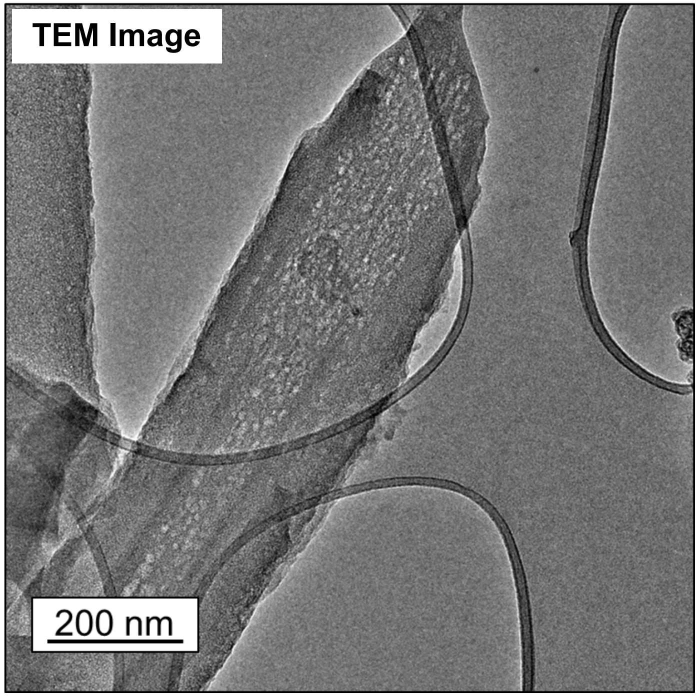
- Fe dissolution rate following redox transition at ca. 0.65 V, with higher rate measured on the negative side of the redox couple potential; no Zn dissolution detected during cycling up to 1.2 V
- No change in ORR activity of (AD)Fe-N-C after 100 potential cycles

Highlight: Fe dissolution rates for (AD)Fe-N-C are >10× lower than for (CM+PANI)-Fe-C(Zn)

Progress: Increased Iron Utilization in PGM-free Catalysts

(AD)Fe-N-C PGM-free catalyst: Homogenous carbon structure

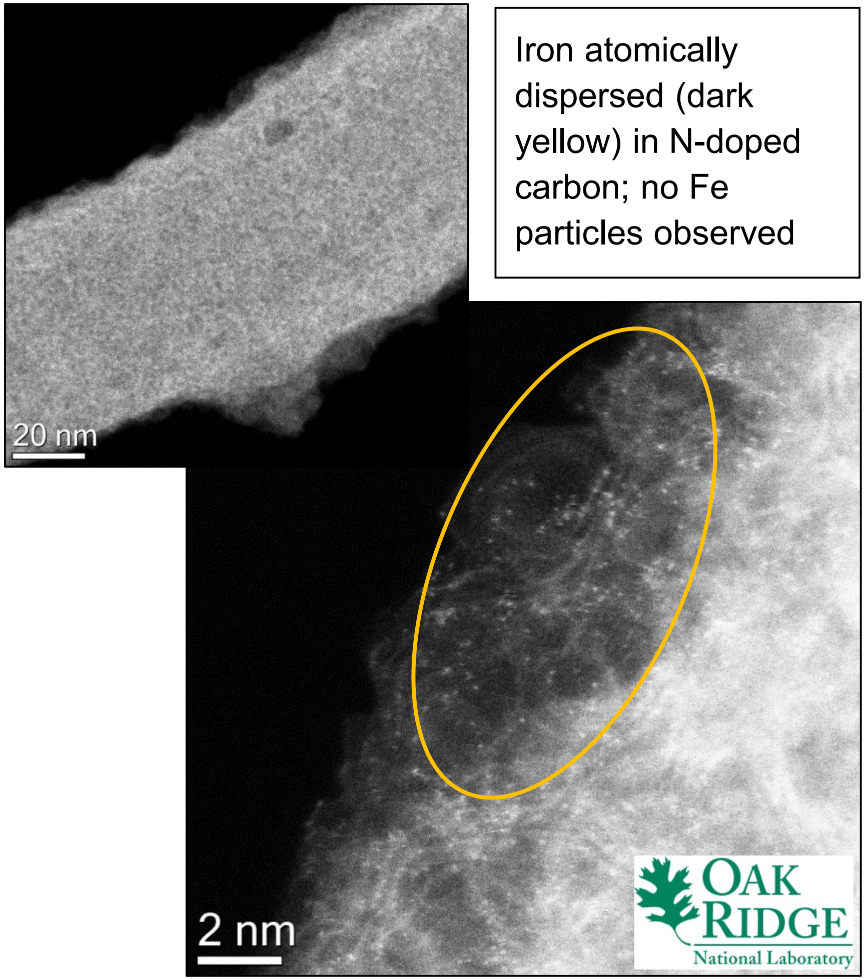




Carbon plates, ~0.2 µm wide and 1.5-2.0 µm long, with enhanced microporosity due to Zn evaporation → much improved accessibility to ORR active sites

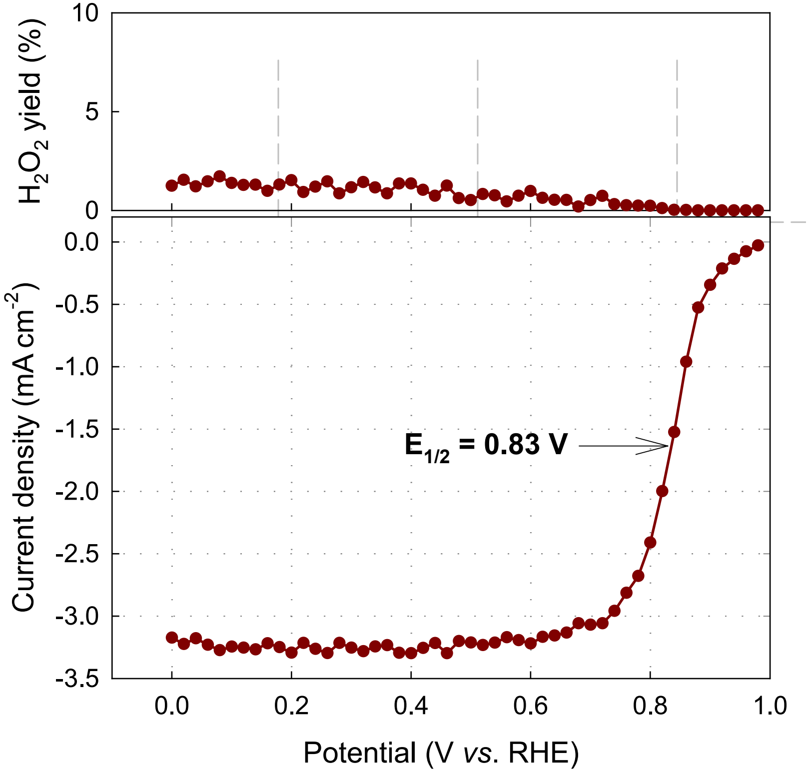
Highlight: No crystalline Fe species observed already after the first heat treatment step → increased Fe utilization

Accomplishment: (AD)Fe-N-C PGM-free ORR Catalyst



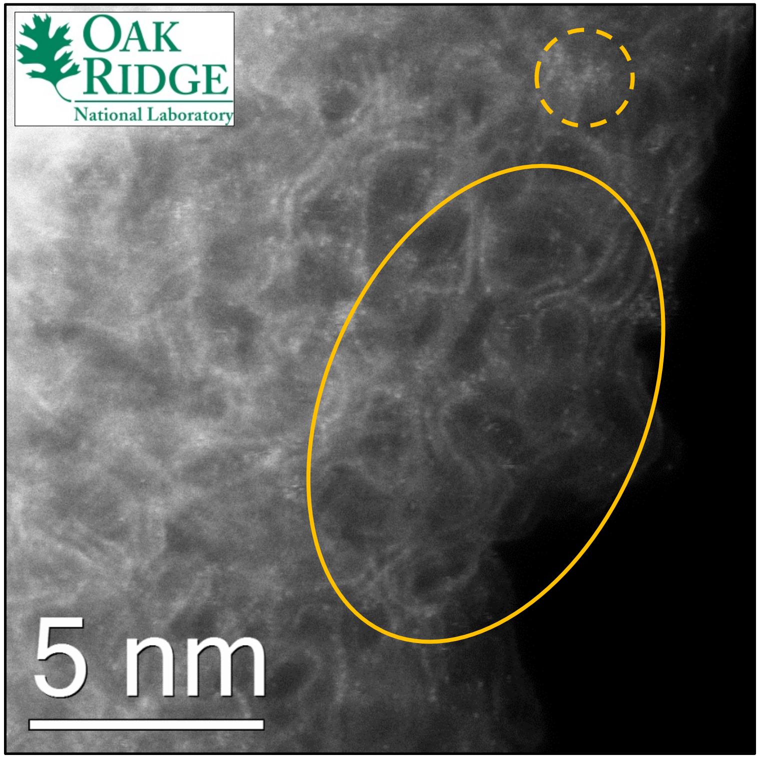
Iron atomically dispersed (dark yellow) in N-doped carbon; no Fe particles observed

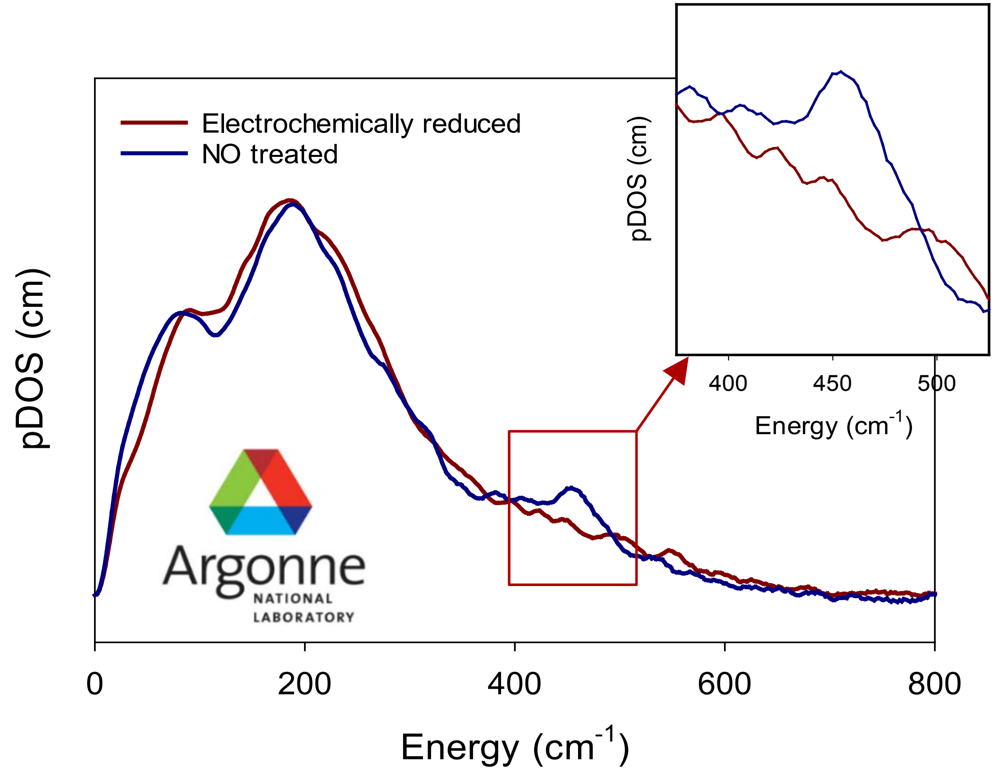
ORR: 0.6 mg cm^{-2}; 0.5 M H_2SO_4; 900 rpm; 25ºC; Hg/$HgSO_4$ (0.5 M H_2SO_4) reference electrode; graphite counter electrode; steady-state potential program: 20 mV steps, 20 s/step;



Highlight: Atomically dispersed Fe catalyst showing very high ORR activity in RDE testing ($E_{½}$ of **0.83 V**) and excellent 4e$^-$ selectivity (H_2O_2 yield **< 1.5 %**)

Accomplishment (Major): Direct Detection of Fe Sites on (AD)^{57}Fe-N-C

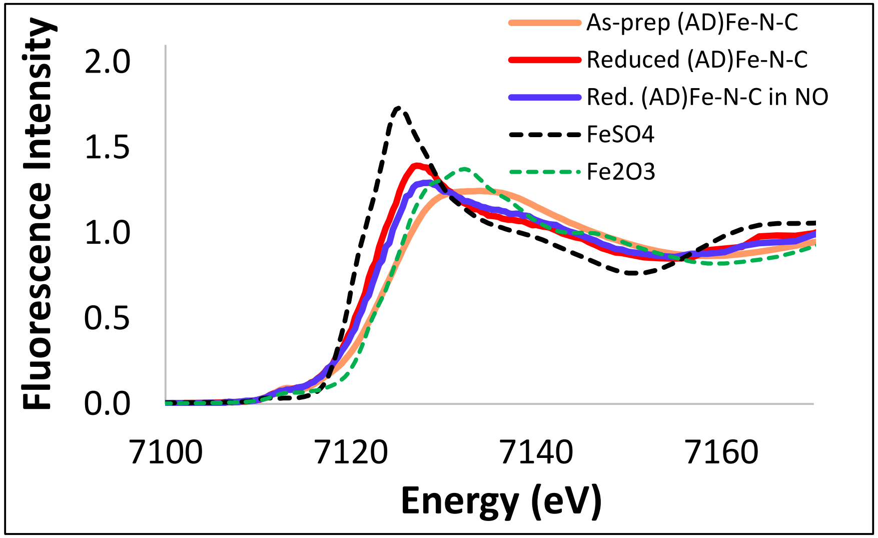


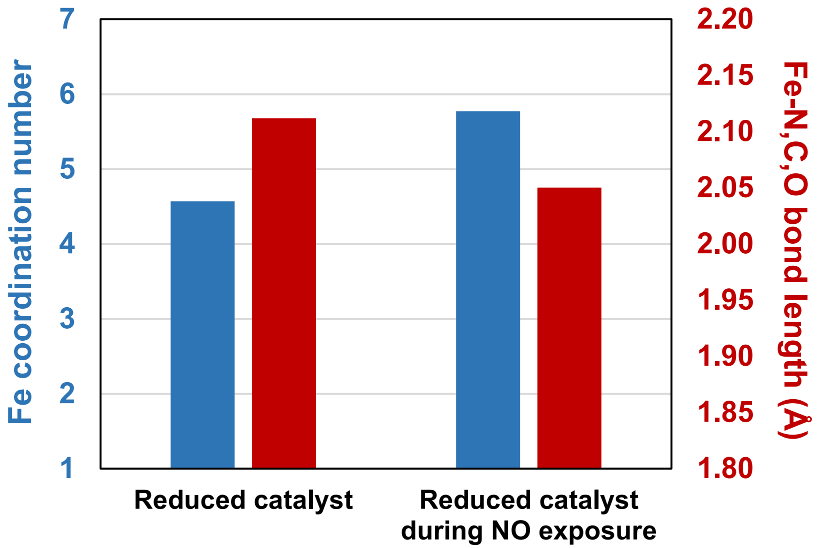


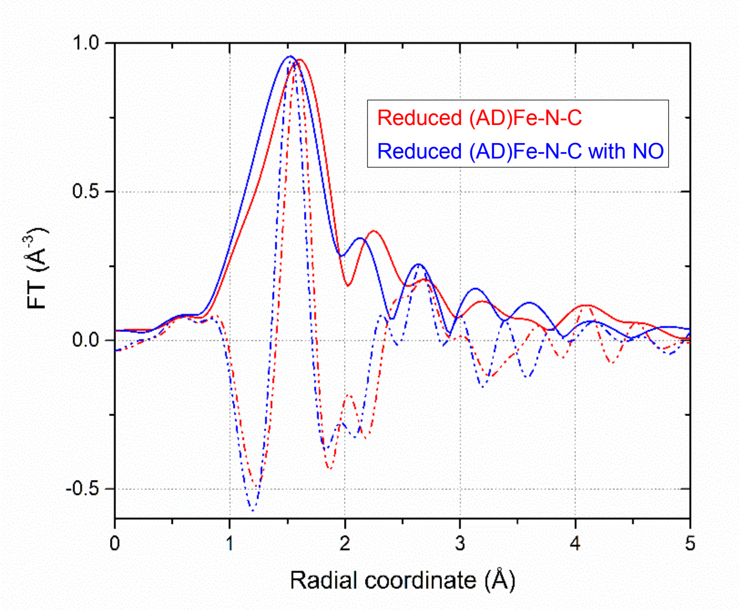
- ^{57}Fe-enriched catalyst demonstrating the same properties as non-enriched catalyst: atomically dispersed iron seen (solid yellow line), with some Fe-clustering (dashed yellow line)
- Nuclear resonance vibrational spectroscopy (NRVS) used with NO as a molecular probe (an O_2 analog) to detect iron sites on (AD)^{57}Fe-N-C catalyst; vibrational feature for NO-treated catalyst at a frequency of 450 cm^{-1}, likely corresponding to the Fe-NO bond stretch (assignment pending)

Highlight: Direct evidence of the presence of Fe sites on the surface of a PGM-free catalyst!

Progress: X-ray Absorption Study of (AD)Fe-N-C Active Site

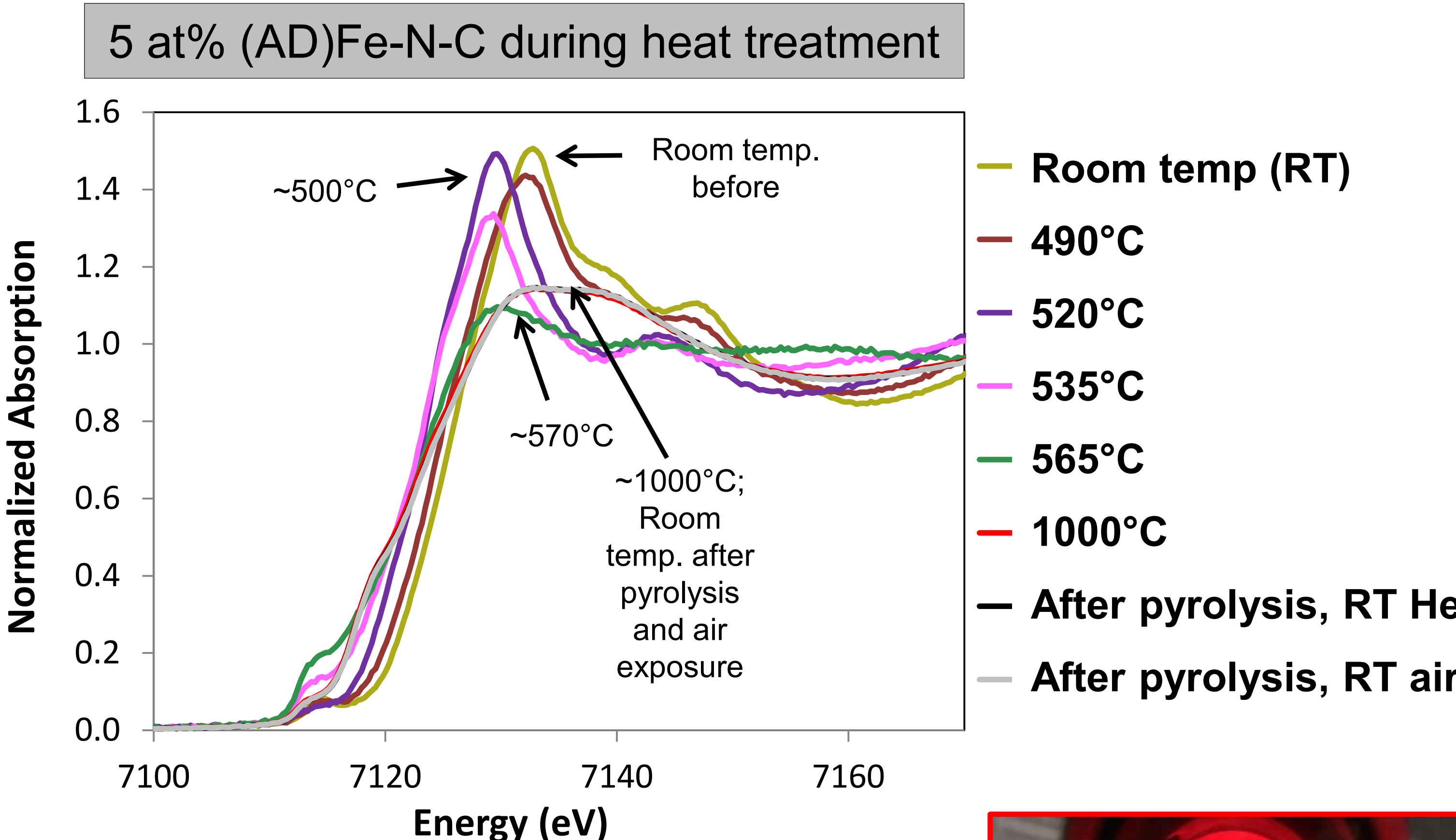




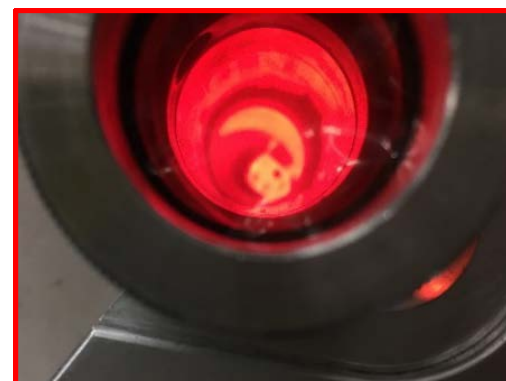


- Fe coordination number in reduced catalyst consistent with predominant composition of four-coordinated Fe-(N,C,O) species
- During NO exposure, coordination number increased by **~1** and bond distance decreased by ~3%
- Coordination number increase of ~1 consistent with the majority of Fe sites coordinating NO (*i.e.*, located on the surface of the catalyst)

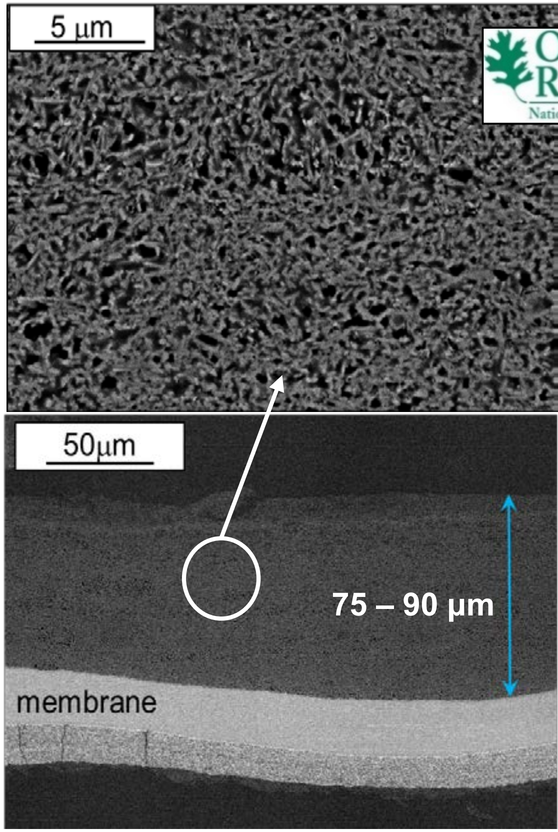
Progress: *In situ* XAFS during Heat Treatment

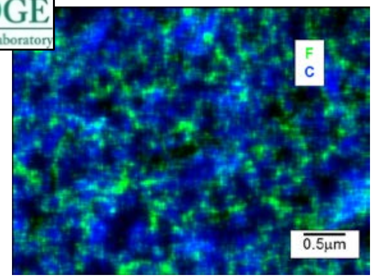


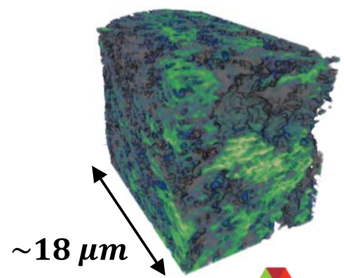
- Six catalysts studied simultaneously
- Precursor highly oxidized at room temperature
- Fe species reduced at ~500°C
- Fe species found in ORR active catalyst formed at ~620-700°C
- Fe species not changing during cooling step or upon exposure to air at room temperature

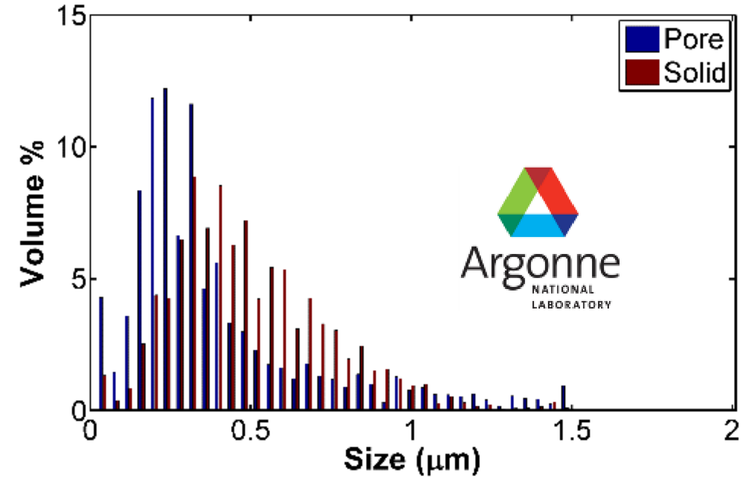


Progress: (AD)Fe-N-C Catalyst Fuel Cell Performance

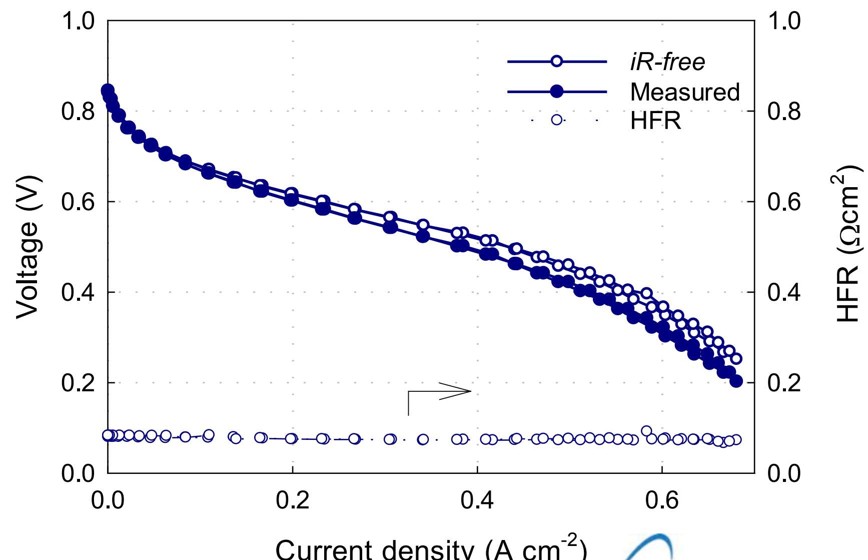








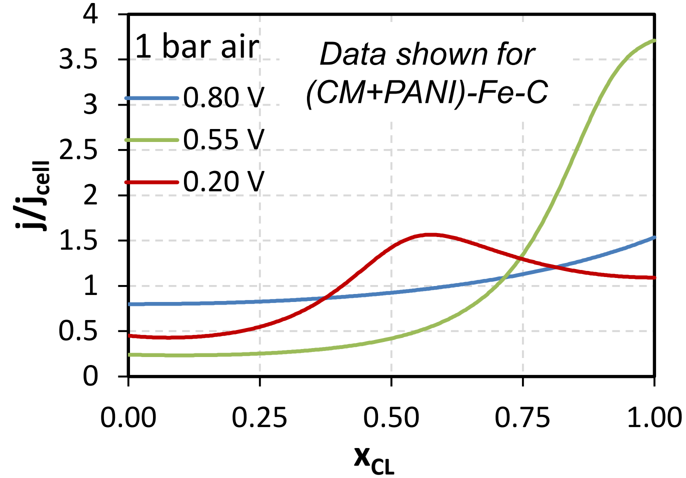
Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode**: 8.0 wt% Co catalyst air, 200 sccm, 1.0 bar air partial pressure; **Membrane**: Nafion®211; **Cell**: 80°C



- Dense (AD)Fe-N-C catalyst layer with uniform distribution of catalyst, but non-optimized ionomer distribution (see ionomer aggregates in fluorine map and nano-CT image)
- Low fuel cell performance caused by dense packing of catalyst layer resulting in uneven ionomer distribution and low porosity

Progress: PGM-free Cathode Catalyst Layer Model

Purpose: Determine cathode properties limiting performance as a function of cell operating conditions and identify means for improving performance



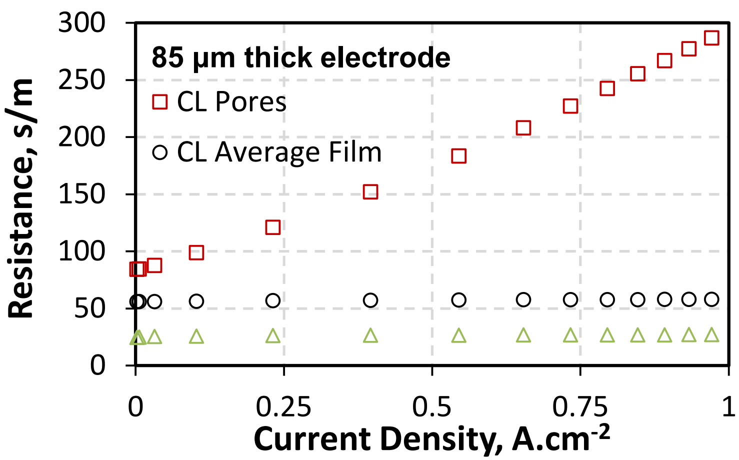
Distributed ORR Kinetics

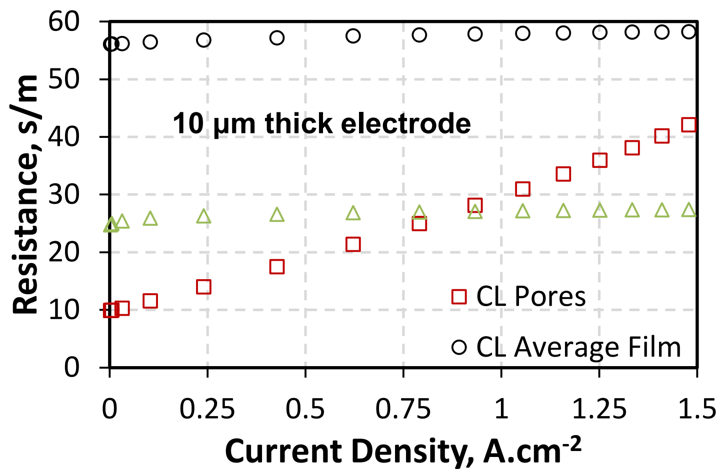
- In pure O_2, ORR mainly confined to the membrane boundary
- In air, ORR zone broadens and shifts towards diffusion media due to transport resistance in pores

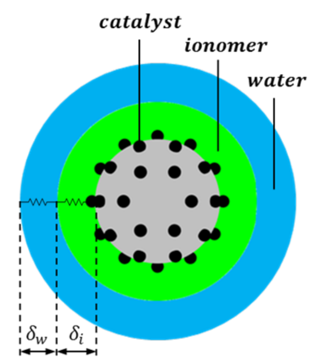
Cathode model for quantification of mass transport losses

- Bundle-of-capillaries model to determine electrode water retention curves

$$\delta_w = \frac{\delta_i \epsilon_v S}{\epsilon_N}$$



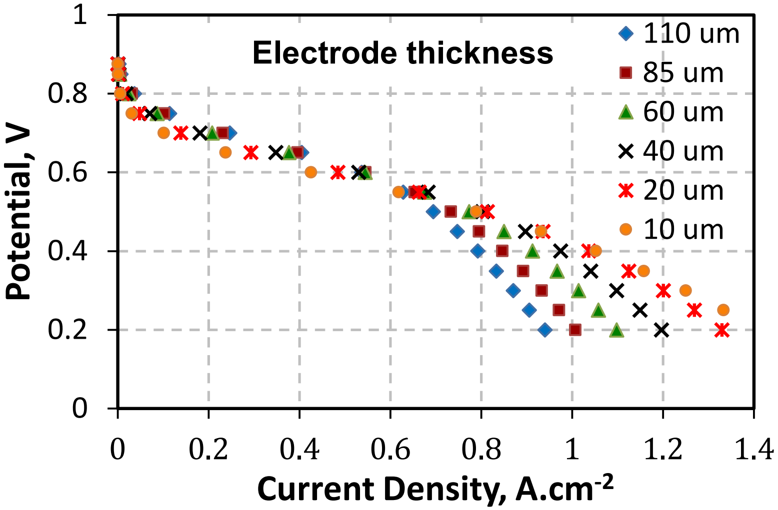


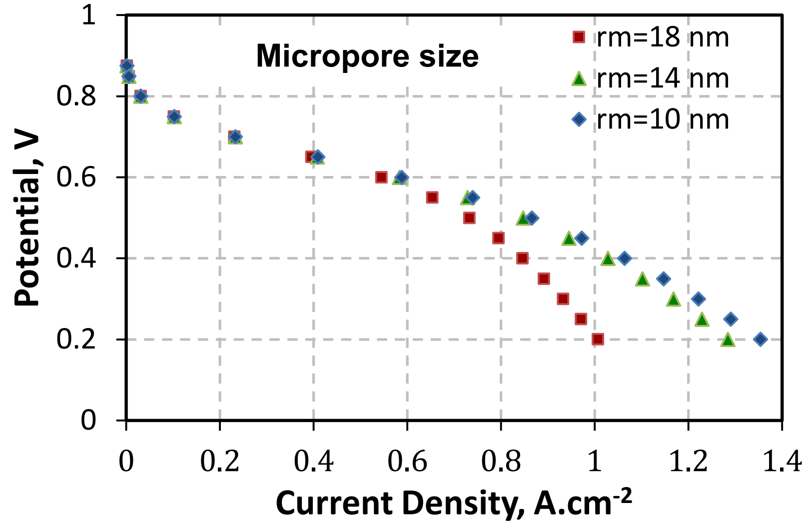


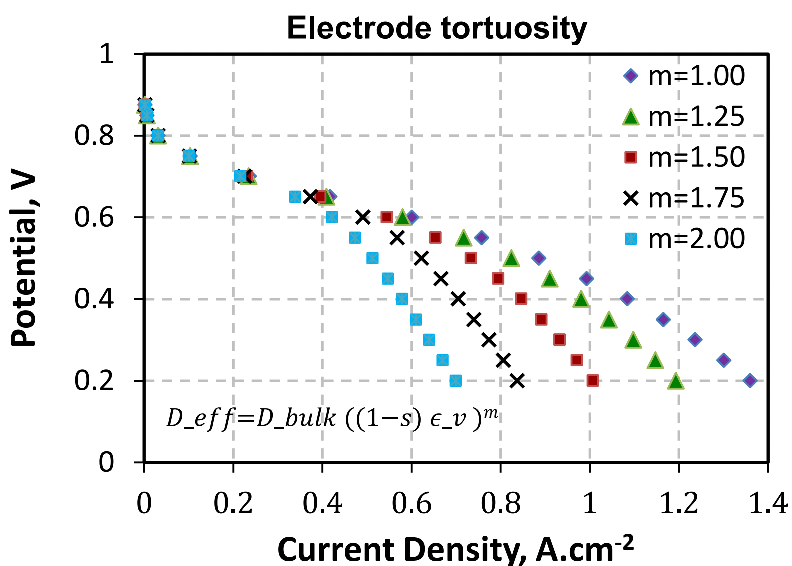
O$_2$ mass transport losses are dominated by flooded pores in thick electrodes and film resistance in thin electrodes

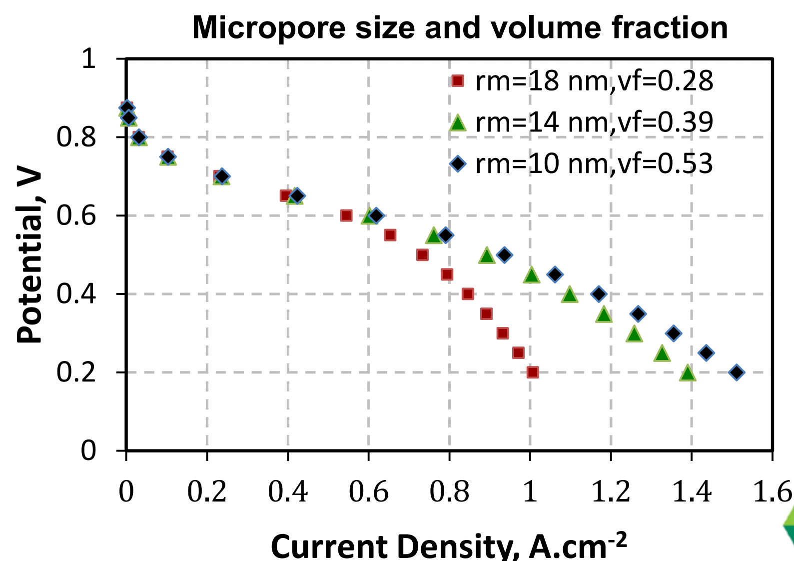
Progress: Methods for Improving High Current Density Performance

Highlight: High current density performance improved by decreasing electrode thickness, tortuosity (m), and size of micropores (rm) and increasing volume fraction (vf) of micropores





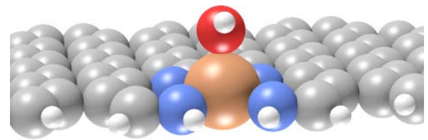




Progress: Durability Descriptor Calculation Automation (DDCA)

(1) Input Structure:

*FeN_4(*OH) - ZZ edge*



(2) Structure Relaxed

ORR Activity Calculations

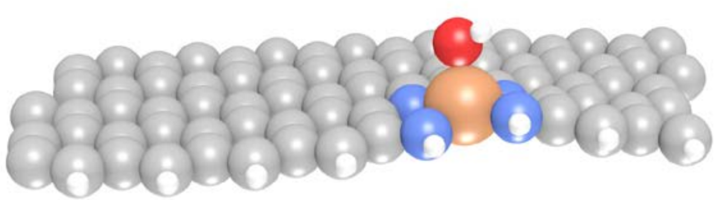
(3) DDCA Setup Script:
input of atoms and energy ranges to test

$$T_{max} = \frac{2ME\left(E+2mc^2\right)}{\left(M+m\right)^2 c^2 + 2ME} \qquad v_{max} = \sqrt{\frac{2T_{max}}{M}}$$

Zobelli, *et al.*, *PRB* **75**, 245402 (2007)

(4) *Ab-initio* Molecular Dynamics (AIMD) Simulations
(100 fs)

(5) DDCA Visualization Script:
generate movies of AIMD calculations in automated fashion



70 kV e^- impacting N of FeN_4 complex at ZZ edge

(6) DDCA Analysis Script:
determine KODTE for each atom

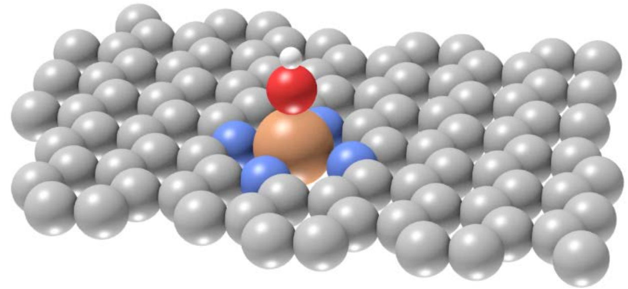
(7) Durability Descriptor for Input Structure

Highlight: Successful automation of setup, calculation/submission, visualization, and durability descriptor analysis

Accomplishment: Establishment of KODTE Library

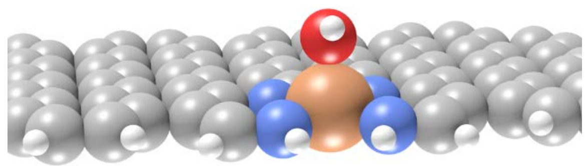
Structure	KODTE (kV)
FeN_4 bulk	90
FeN_4OH bulk	90
MnN_4 bulk	90
MnN_4OH bulk	90
CoN_4 bulk	90
CoN_4OH bulk	90
FeN_4 arm chair	35*
FeN_4OH arm chair	30*
MnN_4 arm chair	35*
MnN_4OH arm chair	25*
CoN_4 arm chair	35*
CoN_4OH arm chair	30*
FeN_4 zig zag	70
FeN_4OH zig zag	70
MnN_4 zig zag	65
MnN_4OH zig zag	70
CoN_4 zig zag	70
CoN_4OH zig zag	75
Fe_2N_5 bulk	60
Fe_2N_5OH bulk	60
$MnCoN_5$ bulk	60
$MnCoN_5OH$ bulk	60
Graphene	110
Arm chair edge	90
Zig zag edge	85

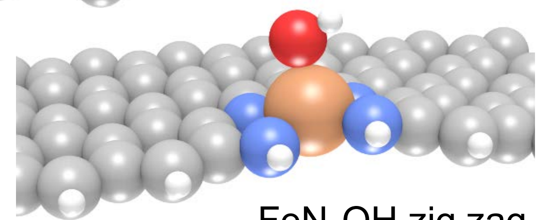
* some but not all bonds broken



FeN_4OH bulk

FeN_4OH arm chair





FeN_4OH zig zag

Findings thus far:

- N most susceptible to e^- beam damage → lowest knock-on displacement threshold energy (KODTE) in all considered cases
- Edge atoms more susceptible than bulk even for carbon supports, edge atom has lowest KODTE
- No large dependence on metal (M) speciation calculated
- No large dependence on *OH ligand calculated
- Need to test N-coordination (MN_3 structure) and other possible structural effects

Highlight: Successful completion of initial set of library calculations for bulk-C structures

Accomplishment: High-throughput Synthesis and Characterization

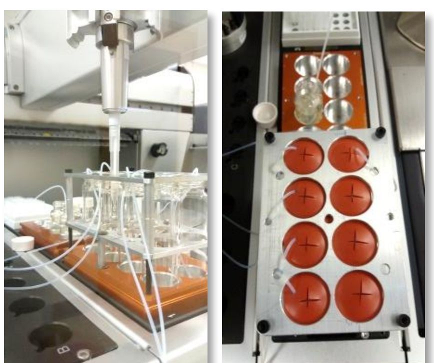
Purpose: Utilize Argonne's robotic system, simultaneous pyrolysis, high-throughput structural characterization using XRD and XAFS, and multi-channel flow double electrode cell for ORR activity characterization to explore catalyst composition and heat treatment effects.

Catalyst system: LANL's (AD)Fe-N-C selected due to high RDE ORR activity

Parameters varied to obtain 40 unique samples:

- ✓ Fe-to-Zn ratio: 0, 1, 2.5, 5, and 7.5 at% Fe in precursors
- ✓ Fe salts: sulfate, nitrate, acetate
- ✓ Heat-treatment temperatures: 900, 1000, 1100°C

Precursor synthesis: CM Protégé Robot

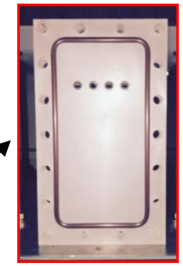


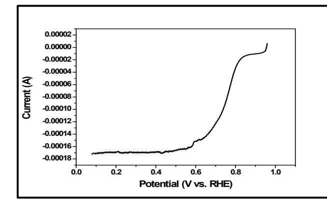
→

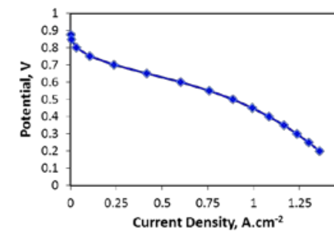
Heat Treatment

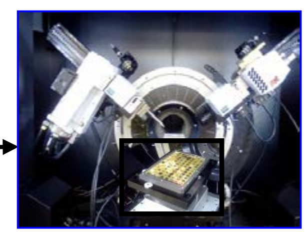
ORR Activity → MEA Performance → Phase Composition → Atomic Structure →

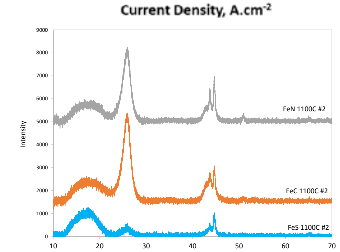
Characterization

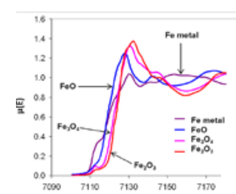




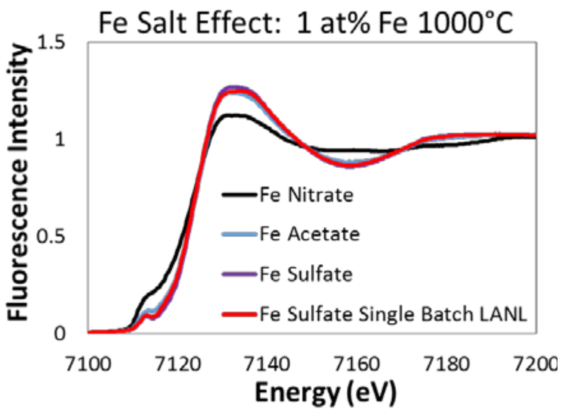


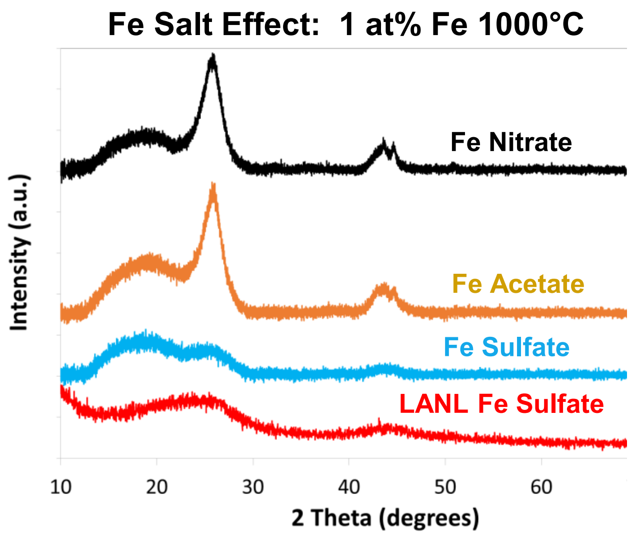


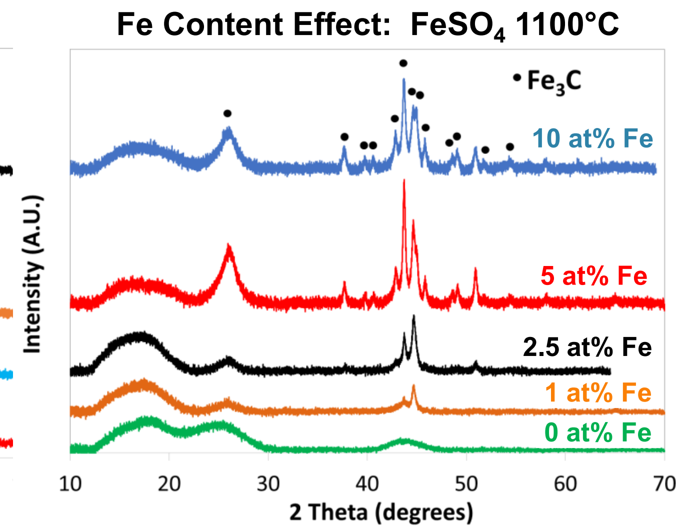


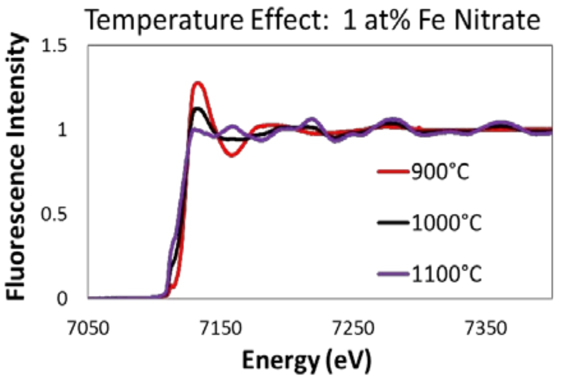


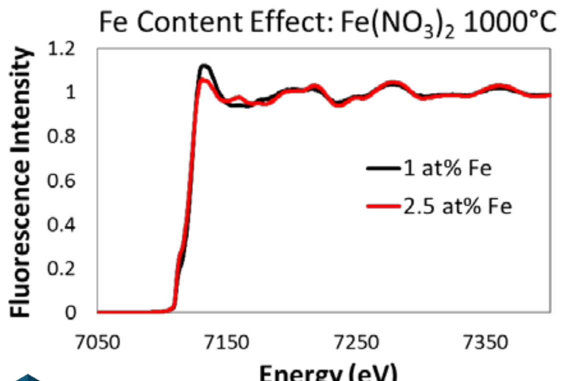
Progress: High-throughput Characterization of (AD)Fe-N-C









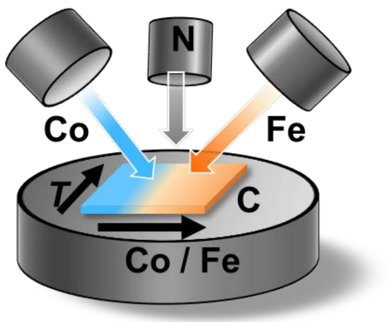


- High-throughput synthesized (AD)Fe-N-C has same Fe XAFS as LANL's (AD)Fe-N-C
- Fe acetate- and Fe sulfate-derived (AD)Fe-N-C have similar atomic structure; Fe nitrate results in Fe species with lower oxidation state
- Pyrolysis temperature and Fe content have a large effect on Fe atomic structure and oxidation state
- Crystalline Fe species formed is Fe carbide; carbide content increases with Fe content and pyrolysis temperature
- **Ongoing steps:** High-throughput hydrodynamic ORR activity measurements; electrode fabrication and testing

Capability Development: Model System Synthesis & Characterization

Purpose: Elucidate the nature of ORR active sites and discover materials with enhanced ORR activity using PGM-free thin films with well-controlled composition and structure

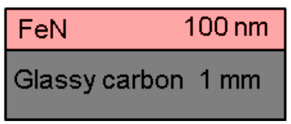
PVD Synthesis



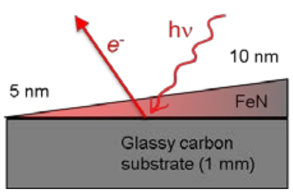
Capability: Combinatorial Synthesis and Spatially-Resolved Characterization

- Multi-element thin films of nanoparticles (metals, oxides, nitrides, sulfides)
- Gradients (composition, temperature, film thickness, nanoparticle size, *etc.*)
- Physical vapor deposition techniques (sputtering, pulsed laser deposition)
- Supports (highly oriented pyrolytic graphite, metals, glass, *etc.*)
- Characterization by XRF, XPS, XRD, *etc.*
- Electrochemical characterization being developed

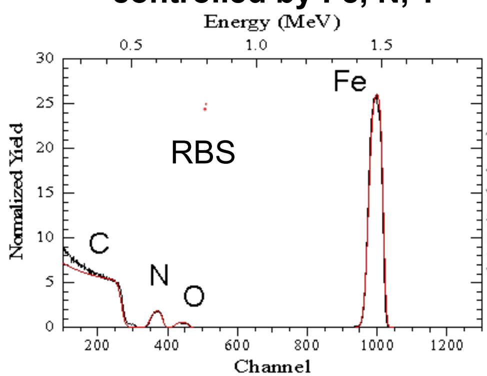
Thick film to determine deposition conditions



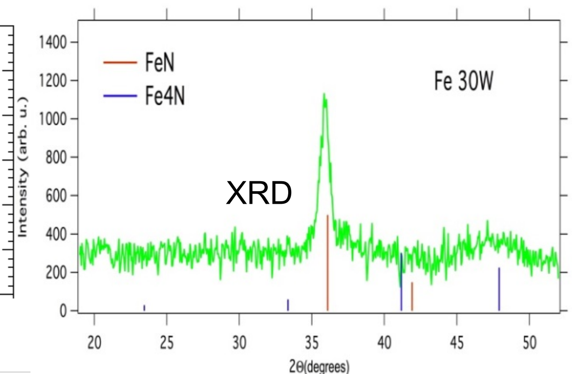
FeN/C interface by thin film deposition

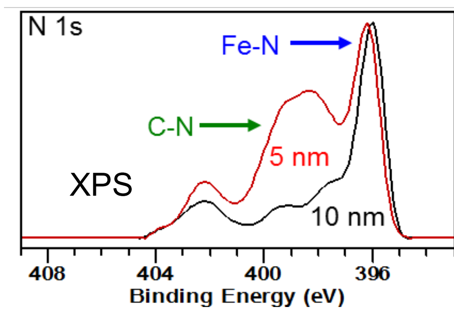


Fe-N composition controlled by Fe, N, T



Tetrahedral FeN formed





- Fe-N bonds present in FeN thin films
- C-N bonds formed at FeN/C interface
- Formation of FeN_4 moiety in carbon matrix likely

Summary: Demonstrated first Fe-C-N model systems with composition similar to active catalysts

Next step: Perform RDE testing of ORR activity to asses catalytic performance of the model systems

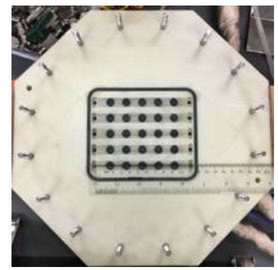
ElectroCat Electrocatalysis Consortium

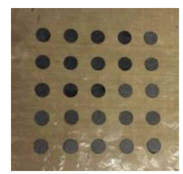
NREL NATIONAL RENEWABLE ENERGY LABORATORY

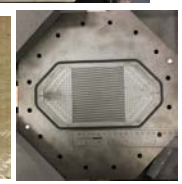
Capability Development: Combinatorial Fuel Cell Performance Testing

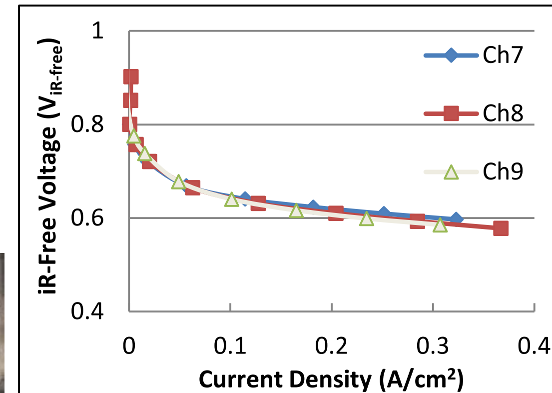
Purpose: Accelerate the optimization of the electrode composition and structure for PGM-free catalysts by developing methods for the high-throughput synthesis and deposition of catalyst-ionomer-solvent inks, and measuring ORR activity and fuel cell performance, using:

- **Combinatorial 25-electrode segmented electrode hardware from NuVant (ANL)**
  - ✓ Demonstrated for measuring ORR activities
  - ✓ Identical *iR*-corrected H_2-air polarization curves for different channels
  - ✓ Resistance uniformity in need of improvement

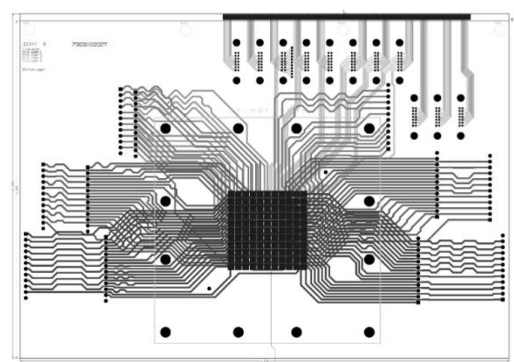


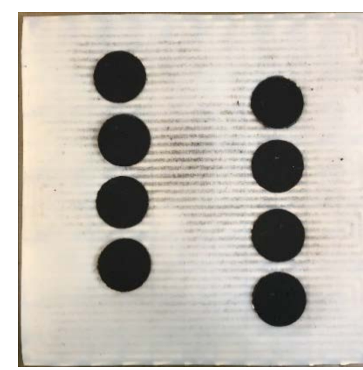






- **Segmented fuel cell hardware (NREL)**
  - ✓ Cross-talk between segments of cell hardware with common GDL quantified
  - ✓ Several approaches investigated to mitigate cross-talk and enhance ability to test combinatorial samples: (i) parallel flow field design; (ii) segmented GDLs; (iii) segmented electrodes





Collaborations

- **ElectroCat members:** Four National Laboratories with highly complementary skills and capabilities in catalyst development and advanced characterization, electrode structure design and modeling, MEA fabrication, and electrochemical and fuel cell testing:
  - ✓ Los Alamos National Laboratory – *ElectroCat Co-lead*
  - ✓ Argonne National Laboratory – *ElectroCat Co-lead*
  - ✓ National Renewable Energy Laboratory
  - ✓ Oak Ridge National Laboratory
- **No-cost collaborators not directly participating in ElectroCat:**
  - ✓ University at Buffalo (SUNY), Buffalo, New York – novel PGM-free catalysts
  - ✓ Technical University Darmstadt, Germany – catalyst characterization by Mössbauer spectroscopy and synchrotron X-ray techniques
  - ✓ CEA – LITEN/DEHT/SCGE, Grenoble, France – MEA optimization and characterization
  - ✓ Fraunhofer ICT, Pfinztal, Germany – PGM-free catalyst corrosion (DEMS studies)
  - ✓ Colorado School of Mines, Golden, Colorado – XPS characterization
  - ✓ University of Warsaw, Poland – PGM-free catalyst corrosion studies (DEMS studies)
  - ✓ Pajarito Powder, LLC, Albuquerque, New Mexico – catalyst scale-up and commercialization (license of a LANL PGM-free catalyst in 2016)
  - ✓ Chevron Energy Technology Company, Richmond, Californi*a* – CRADA on non-electrochemical applications of PGM-free carbon-based materials

Summary

- **ElectroCat** launched in February 2016: effort initially focused on consortium development, followed by PGM-free catalyst and electrode R&D and capability demonstration and development for last nine months
- **Consortium Development**
  - ✓ National laboratories with capabilities relevant to PGM-free catalyst development and implementation were selected and Steering Committee established
  - ✓ A public ElectroCat website was inaugurated in February 2016 and the national laboratory capabilities posted (www.ElectroCat.org)
  - ✓ A data management hub was established based on Globus and leveraging the Materials Data Facility data publication capabilities
  - ✓ A streamlined CRADA template and NDA completed, approved, and is available for use
- **Performance Improvement**
  - ✓ Demonstrated hydrogen-air performance of 120 mA/cm^2 at 0.8 $V_{iR\text{-}free}$ with (CM+PANI)-Fe-C(Zn) cathode catalyst, a 25% improvement over the 2016 status
  - ✓ Achieved half-wave potential ($E_{½}$) of 0.83 V with (AD)Fe-N-C in RDE testing, an increase of 0.02 V over the 2016 status
  - ✓ PGM-free catalyst activity in an MEA: 16 mA/cm^2 at 0.90 $V_{\text{iR-free}}$ and 0.044 A/cm^2 at 0.87 V
- **Characterization and Capability Development**
  - ✓ Determined >10× lower Fe dissolution rate with (AD)Fe-N-C than (CM+PANI)-Fe-C(Zn)
  - ✓ Obtained direct evidence of a majority of Fe sites being atomically-dispersed and on the (AD)Fe-N-C catalyst surface using TEM, a molecular probe and X-ray spectroscopies

Summary (Continued)

- ✓ Using TEM and nano-CT, elucidated the source of performance limitations and identified pathways to improving (AD)Fe-N-C fuel cell performance
- ✓ Synthesized 40 variations of (AD)Fe-N-C catalyst and characterized atomic structure using high-throughput X-ray diffraction and spectroscopy

- **Characterization and Capability Development**
  - ✓ Synthesized and characterized the composition of model thin-film FeN/C catalyst
  - ✓ Obtained 9 mV ORR half-wave potential agreement for Pt/C and < 30 mV agreement for PGM-free catalyst between RDE and multi-channel flow double electrode measurements
  - ✓ Developed and utilized the capability to characterize by XAFS the atomic structure of catalysts during heat treatment
  - ✓ Developed a PGM-free cathode performance model considering the effects of flooding, mass, and charge transfer and applied it to the (CM+PANI)-Fe-C cathode
- **ORR active-side activity and durability modeling**
  - ✓ Developed durability descriptor calculation automation (DDCA) approach to determine the values of knock-on displacement threshold energy (KODTE), a durability descriptor
  - ✓ Completed the initial set of 25 KODTE values for various metal-N_4 sites in the bulk and on arm-chair and zig-zag edges of graphene sheets in PGM-free catalysts
- **Project performance measures**
  - ✓ ElectroCat milestones and quarterly progress measures (QPMs) for all four labs either completed or on track

Remaining Challenges and Barriers

- Oxygen reduction reaction activity of PGM-free ORR catalysts in continued need of further improvement to reduce cathode thickness and lower cost of other stack components
- Insufficient long-term stability and performance durability under steady-state and load-cycling conditions
- Limited understanding of the ORR mechanism, nature of the ORR active site and mechanism of catalyst degradation preventing rational design of next-generation PGM-free catalysts
- Low volumetric density of active sites
- Electrode design and component integration to provide adequate ionic, electronic, and mass transport to and from active sites
- Replacement of Fe in catalyst with another PGM-free transition metal not catalyzing hydroperoxy radical formation and ionomer degradation
- Integration with existing automotive fuel cell stack and system technology

Future Work

- **Consortium Development**
  - ✓ Incorporate collaborators from DE-FOA-0001647 into ElectroCat and coordinate activities of all ElectroCat partners;
  - ✓ Update ElectroCat website with information from FOA projects, status of capabilities, publications;
  - ✓ Implement capabilities to mint DOIs and other identifiers with persistent landing pages for datasets and to support automated data capture and publication;
  - ✓ Document ElectroCat Data Sources: **(i)** formats, **(ii)** associated metadata, **(iii)** sharing needs, and **(iv)** dataset comparison or integration needs;
  - ✓ Execute intellectual property management plan and material transfer agreements.
- **Performance and Durability Improvement**
  - ✓ Advance activity of atomically dispersed catalysts by maximizing concentration and accessibility of active centers through **(i)** the development of novel synthesis approaches, **(ii)** optimization of hierarchical pore-size and ionomer distribution, and **(iii)** decreasing electrode tortuosity
  - ✓ Explore (AD)Fe-N-C parameter space for improved performance and durability using high-throughput activity, durability, and performance testing of 40 materials synthesized to date
  - ✓ Determine primary factors governing the durability of PGM-free catalysts, concentrating predominantly on homogenous and thus easier to study materials
  - ✓ Further develop surface-specific methods for the ORR active-site determination

Any proposed future work is subject to change based on funding levels

Future Work (Continued)

- **Characterization and Capability Development**
  - ✓ Active site identification, influence of Fe-N-C ratio on ORR activity, and influence of synthesis parameters on active site formation: **(i)** thin-film model systems; **(ii)** *ex situ*, *in situ*, and operando X-ray spectroscopies and electron microscopy; **(iii)** high-throughput catalyst synthesis, characterization, and activity testing.
  - ✓ ORR kinetics and mechanisms: **(i)** in-cell kinetic measurements as a function of oxygen partial pressure, temperature, cell voltage, *etc.,* **(ii)** electrochemical techniques in aqueous electrolytes.
  - ✓ Degradation mechanisms/durability: **(i)** on-line ICP-MS-RDE to correlate active with catalyst component loss; **(ii)** *ex situ* and *in situ* tomography, spectroscopy, and microscopy; voltage-loss analysis using polarization curves and impedance spectroscopy.
  - ✓ Electrode optimization: **(i)** segmented cell combinatorial studies of electrode performance coupled with high-throughput catalyst-ink synthesis and deposition; **(ii)** tomography and electron microscopy/EDX visualization of solid, pore, and ionomer distribution coupled with electrode transport modeling
- **ORR active-side activity and durability modeling, including high-throughput**
  - ✓ Improved, automated analysis scripts
  - ✓ Application to variety of structures
  - ✓ Analysis of “poisoning” effects of different moieties by comparison to *OH binding energy

Any proposed future work is subject to change based on funding levels

Co-Authors

PGM-free catalyst development, electrochemical and fuel cell testing, atomic-scale modeling

Piotr Zelenay (PI), Laura Barber. Hoon Chung, Edward Holby, Siddharth Komini Babu, Ling Lin, Ulises Martinez, Geraldine Purdy, Xi Yin

High-throughput techniques, mesoscale models, X-ray studies, aqueous stability studies

Debbie Myers (PI), Nancy Kariuki, Magali Ferrandon, Ted Krause, Jaehyung Park, Dali Yang, A. Jeremy Kropf, Rajesh Ahluwalia, C. Firat Cetinbas, Voja Stamenkovic, Eric Coleman, Haifeng Lv, Pietro Papa Lopes, Ian Foster, Ben Blaiszik, Liz Jordan

Catalyst modification, model catalyst development, advanced fuel cell characterization

Huyen Dinh (PI), Yun Xu, Andriy Zakutayev, Thomas Gennett, K.C. Neyerlin, Guido Bender, Michael Ulsh, Kristin Munch, Robert White, Eric Payne

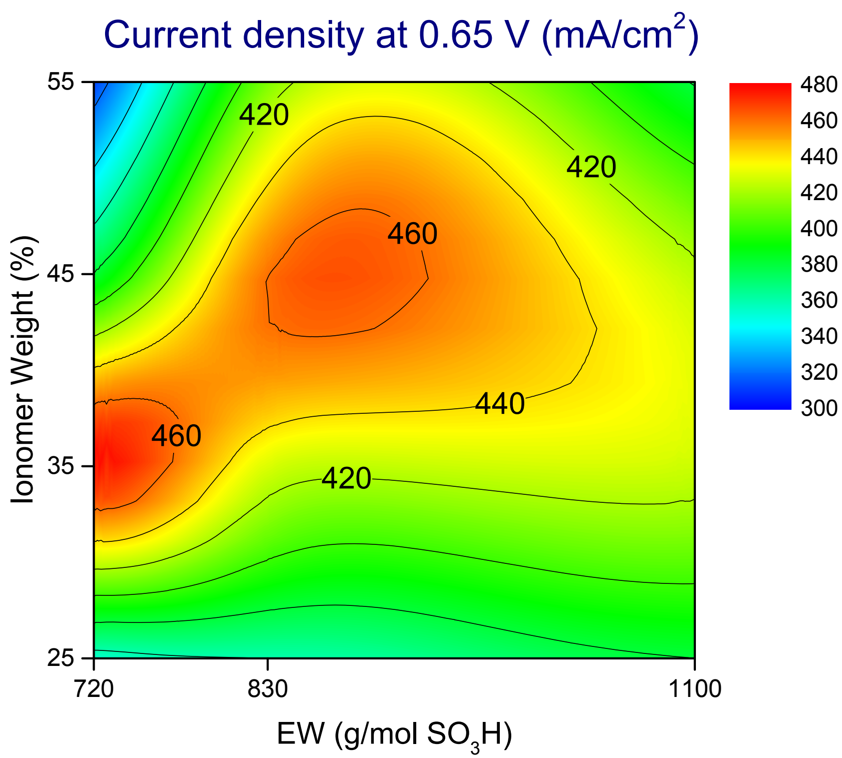
Advanced electron microscopy, atomic-level characterization, XPS studies

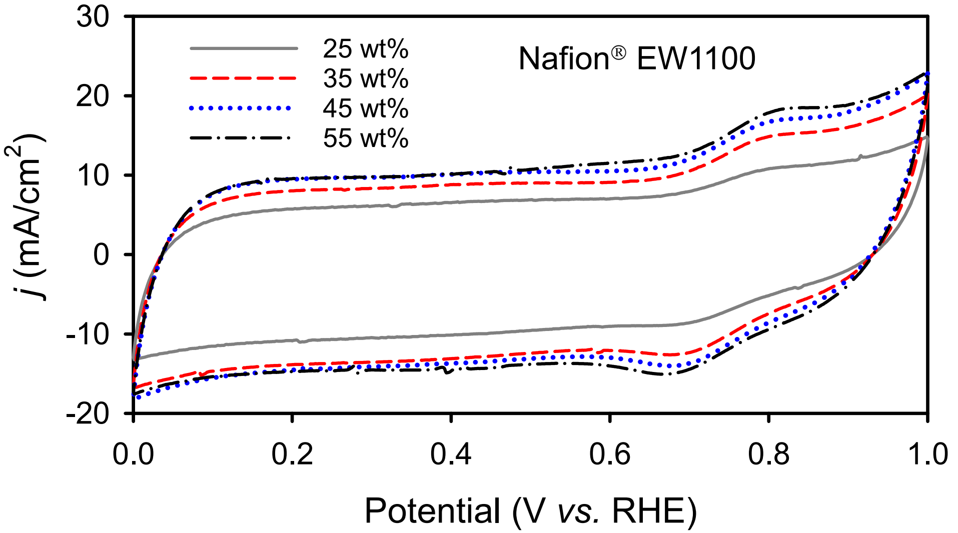
Karren More (PI), David Cullen, Harry Meyer III, Brian T. Sneed

Technical Back-Up Slides

Progress: Effect of EW and Ionomer Content on Catalyst Performance

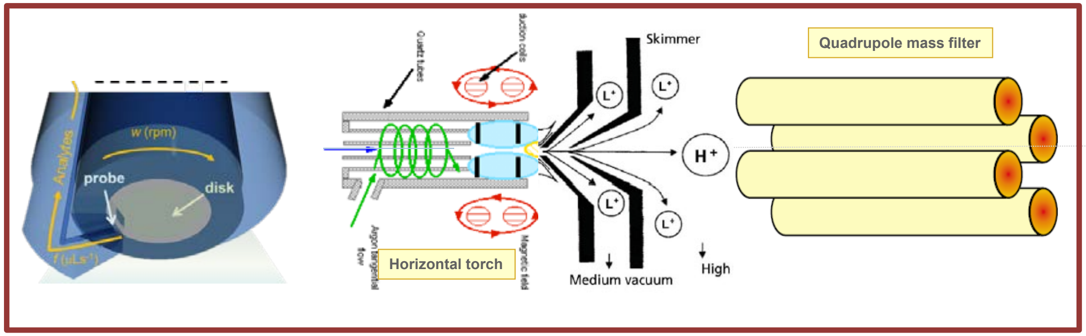
Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** (CM+PANI)-Fe-C(Zn) *ca.* 4.8 mg cm^{-2} (no hot-pressed), air, 200 sccm, 1.0 bar air partial pressure; **Ionomers:** Nafion® D521 (EW 1100), Aquivion® D83 (EW 830), Aquivion® D72 (EW 720); **Membrane:** Nafion®211; **Cell:** 5 cm^2, 80 °C





- Current density at 0.65 V used as a descriptor of fuel cell performance of (CM+PANI)-Fe-C(Zn) catalyst
- Based on the voltammetric response, higher catalyst utilization achieved with higher ionomer content
- Performance at 0.65 V correlating well with catalyst utilization (electrochemical surface area)

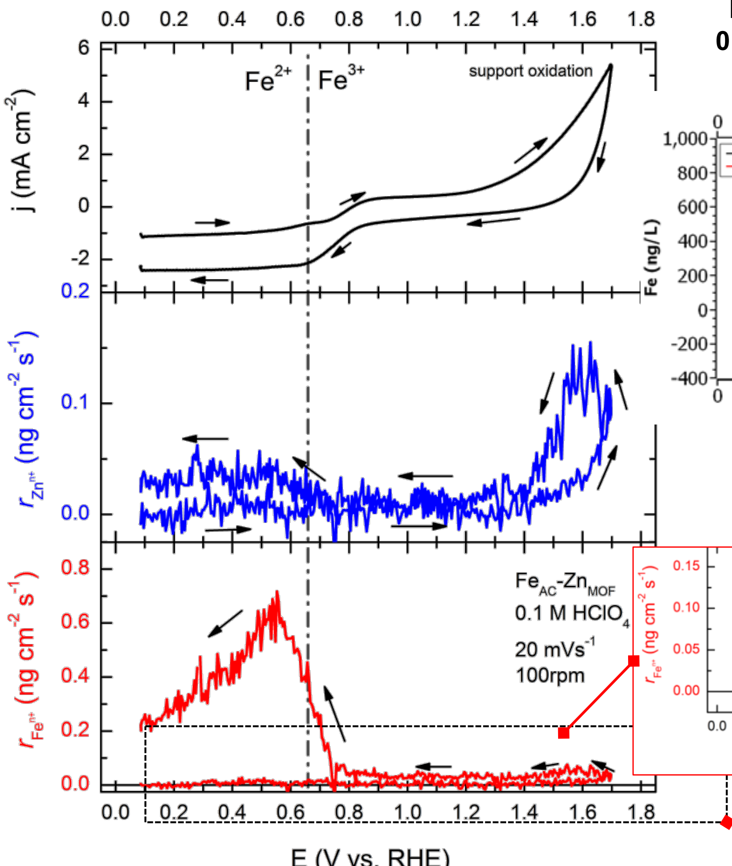
Accomplishment: *In Situ* RDE-ICP/MS of PGM-Free Catalysts

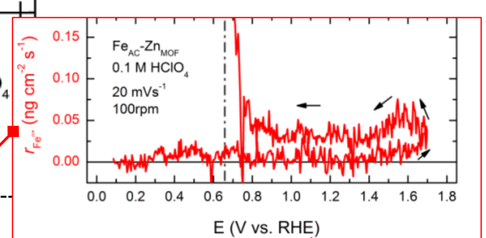


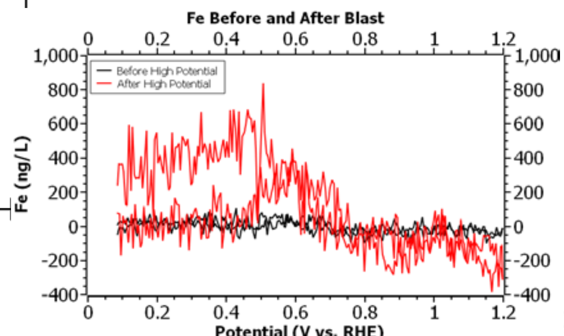
- Stability of PGM-free catalyst is significantly affected by high potential excursions (start-stop conditions)
- Dissolution of Zn occurs at potentials greater than 1.4 V
- Small but measurable Fe dissolution occurs at high potentials together with Zn dissolution
- Substantial increase in iron dissolution in Fe^{3+}/Fe^{2+} redox region - more than observed before scan to 1.7 V

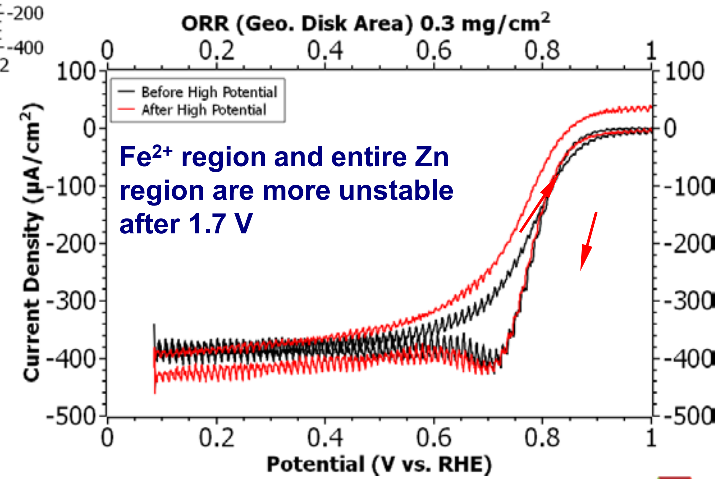
Loading:
0.3 mg/cm²

Potential limit:
0.08 to 1.7 V vs. RHE



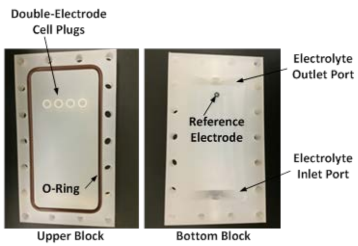


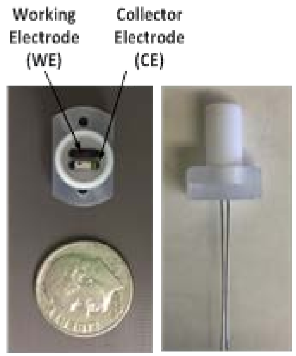




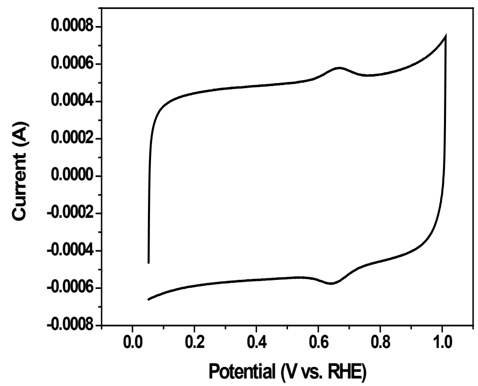
LANL (AD)Fe-N-C: 2.5 at% Fe, 1100°C, H_2SO_4-treated

Progress: Combinatorial Hydrodynamic Screening of Catalyst Activity

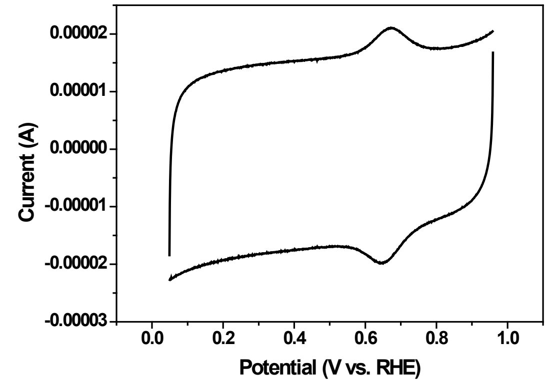




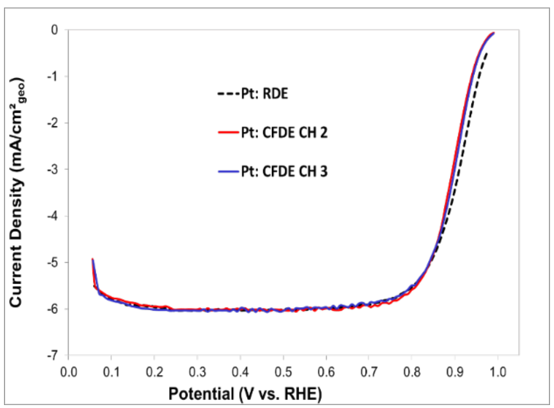
RDE Background



M-CFDE Background

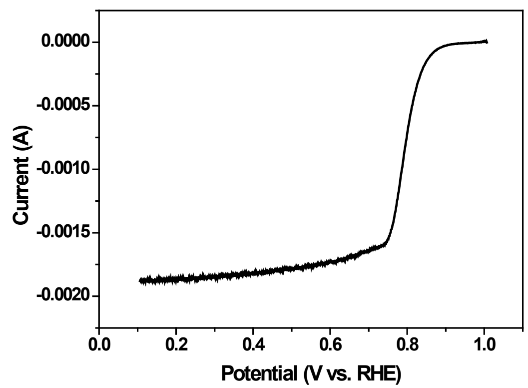


0.6 mg/cm² of LANL's (CM+PANI)-Fe-C(Zn) catalyst; 0.5 M H_2SO_4

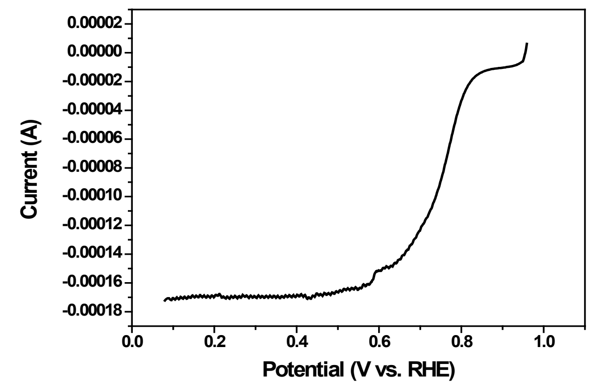


ORR, 18 $\mu g_{Pt}/cm^2$ TKK 46 wt% Pt/C catalyst, 0.1 M $HClO_4$

RDE ORR



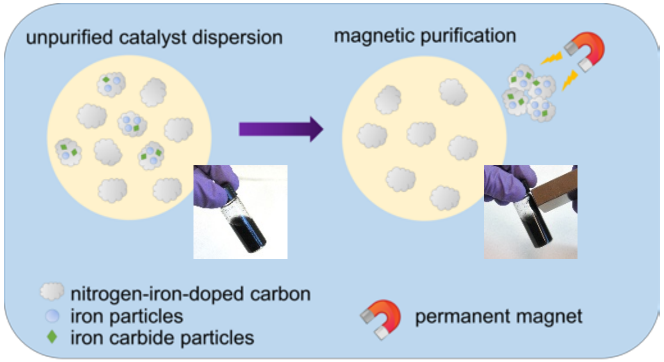
M-CFDE ORR



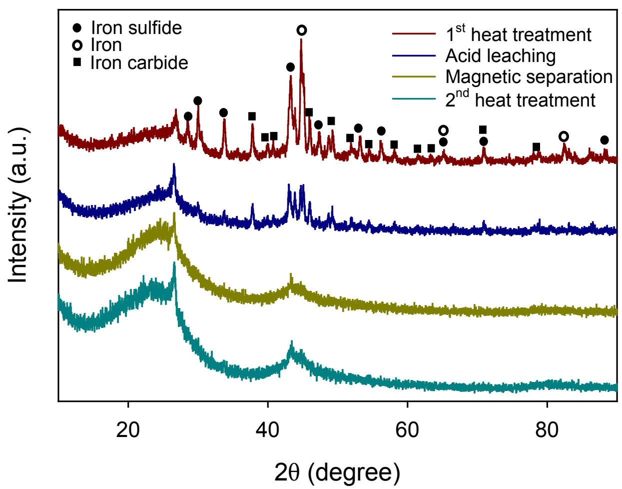
Multi-channel double electrode cell (m-CFDE) $E_{½}$ agrees with RDE to 30 mV for PGM-free catalyst and within 9 mV for PGM catalyst. Automated deposition will improve agreement.

Accomplishment: Magnetic Purification of PGM-free Catalyst

Magnetic purification procedure

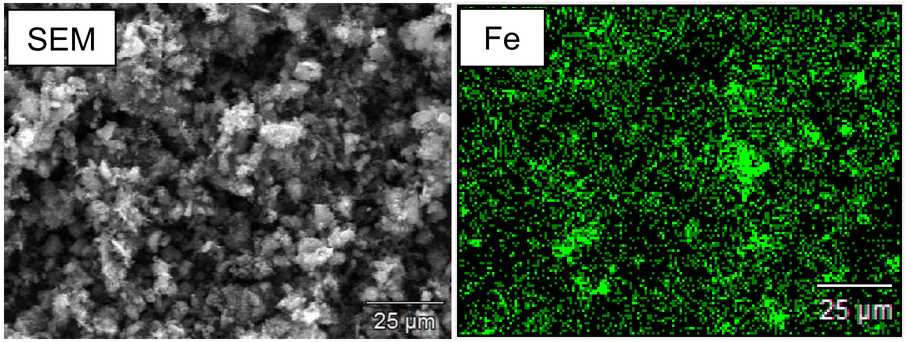


XRD of the magnetic purification process: removal of spectator crystalline Fe species

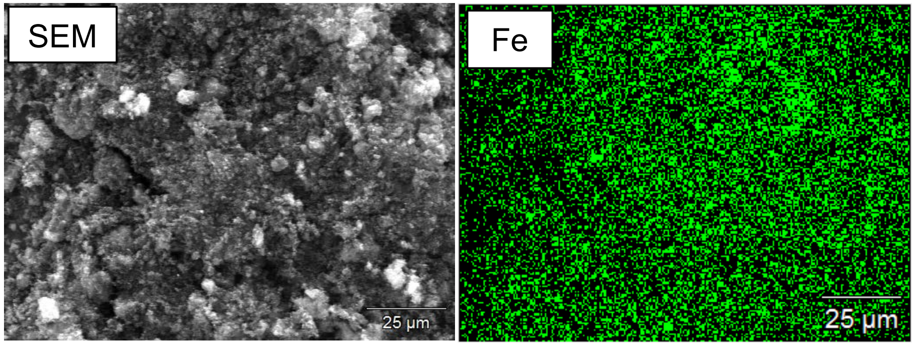


SEM and EDS mapping Fe of the magnetic purification process

Before magnetic purification



After magnetic purification

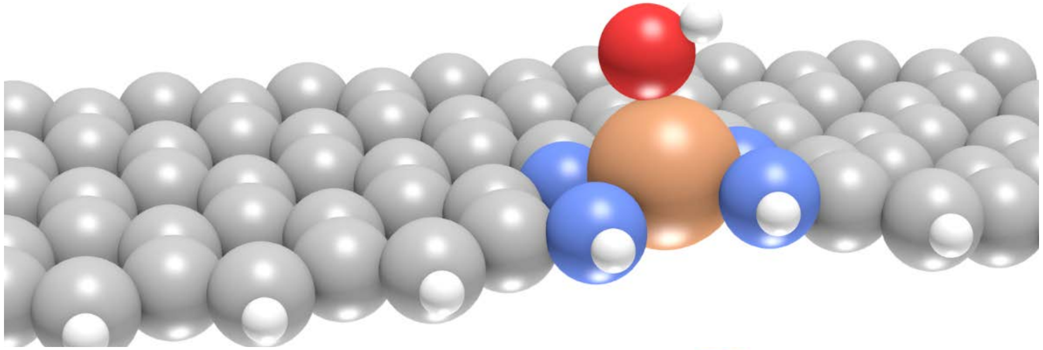


- Large spectator magnetic Fe species effectively removed by magnetic purification
- Well-dispersed Fe in catalyst achieved after magnetic purification

Progress: Activity Descriptor Calculation Automation Developed

Successful automation of efficient structure relaxation via MAST toolkit

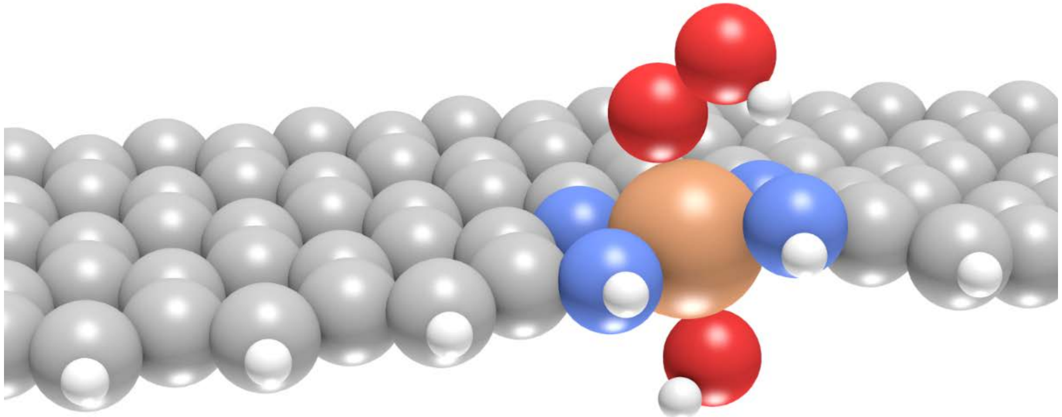
- Future version to script adsorbate placement, pull calculated energies from output files, and print U_L and potential determining step to file



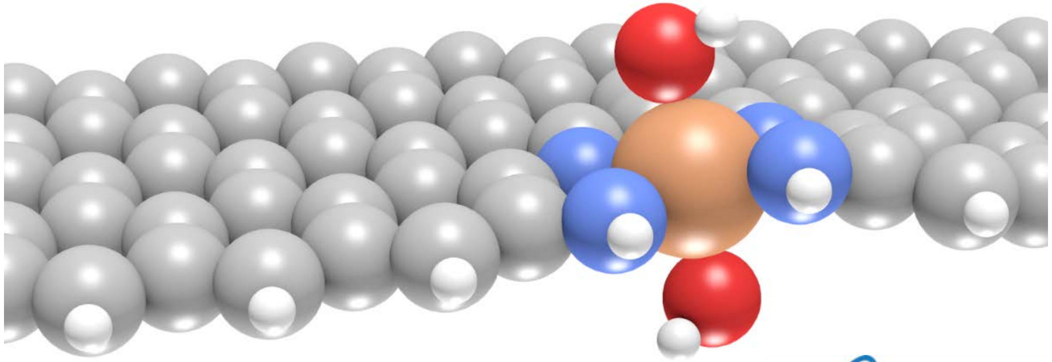
- Application to *bulk-hosted* structures
  - ✓ **MN_4** (M = Mn, Fe, Co)
  - ✓ **MN_4(*OH)** (M = Mn, Fe, Co)
  - ✓ **M_2N_5** (M = Fe_2, MnCo)
  - ✓ **M_2N_5(*OH)** (M = Fe_2, MnCo)

- Application to *AC-edge-hosted* structures
  - ✓ **MN_4** (M = Mn, Fe, Co)
  - ✓ **MN_4(*OH)** (M = Mn, Fe, Co)

- Application to *ZZ-edge-hosted* structures
  - ✓ **MN_4** (M = Mn, Fe, Co)
  - ✓ **MN_4(*OH)** (M = Mn, Fe, Co)

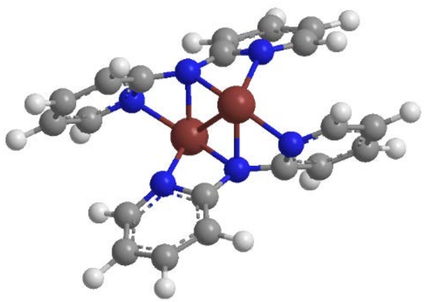


- **Next Steps:**
  - ✓ Improved, automated analysis scripts
  - ✓ Application to variety of structures
  - ✓ Analysis of “poisoning” effects of different moieties by comparison to *OH binding energy

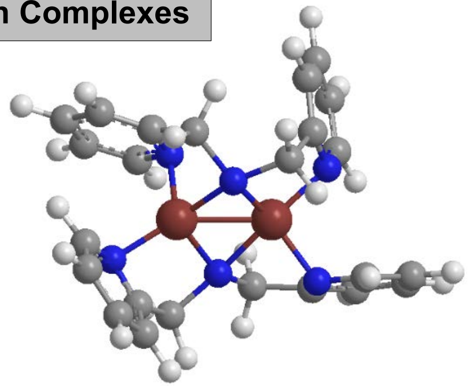


Progress: Catalysts based on Di-iron Complexes

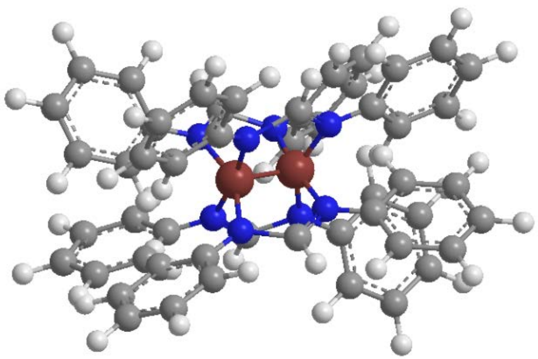
Evaluated Di-iron Complexes



Fe-DPDA

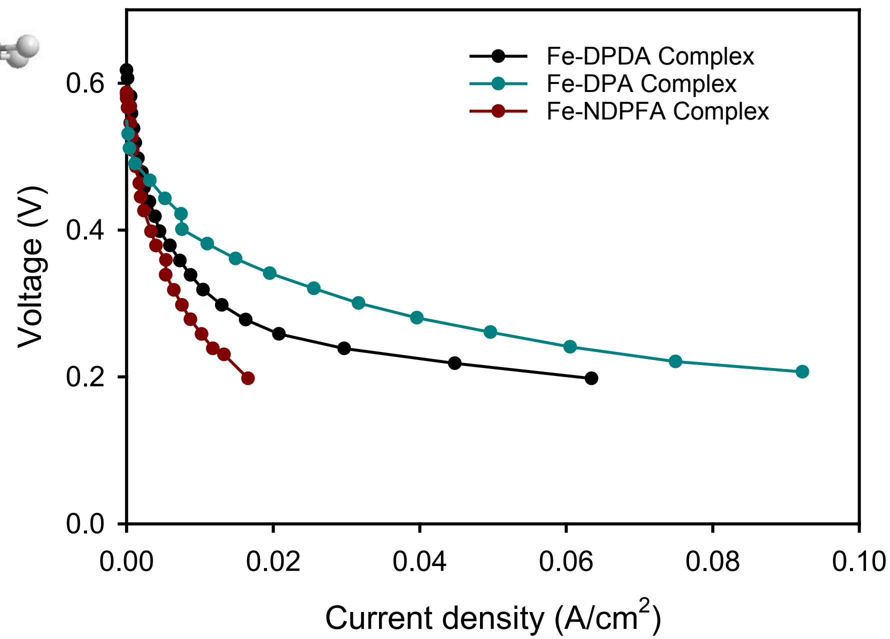


Fe-DPA



Fe-NDPFA

Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 30 psig back pressure; **Cathode:** *ca.* 4.8 mg cm^{-2} air, 500 sccm, 30 psig pressure; **Membrane:** Nafion®211; **Cell:** 5 cm^2, 80 °C



- Several Di-iron complexes synthesized and tested as adsorbates on a carbon support
- Further development stopped after poor performance measured in a fuel cell (LANL QPM FY17 Q2)

Progress: (CM+PANI)-Fe-C Catalyst Performance in O_2 and Air

MEAs with (CM+PANI)-Fe-C cathode catalyst, SGL 24BC diffusion media

- Anode: 0.2 mg_{Pt}/cm^2 Pt/C, Cathode: ~4 mg cat/cm^{-2}, Membrane: Nafion 211, Cell active area: 5 cm^2
- Cathode electrode thickness: 85 ± 5 µm; Ionomer: 35 wt.%, 17.3 vol.%; Catalyst (Fe+C): 65 wt%, 35.7 vol%; Porosity (XCT) 47%; I/C: 0.54
- 0.044 A/cm^2 at 0.87 V (iR-free) in H_2-O_2 at 1 bar P(O_2); 69-88 mV/dec apparent TS

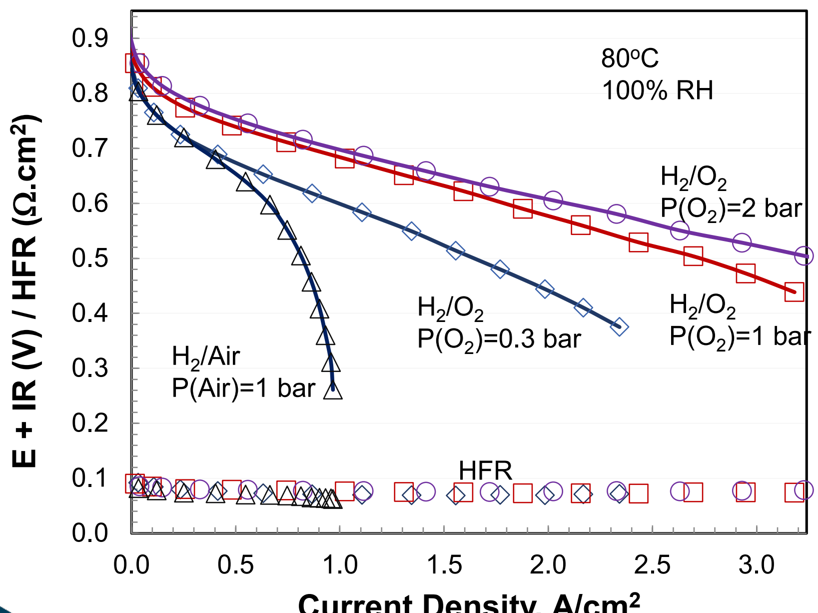
*Pt/C, a-Pt/C, and d-PtNi from Johnson Matthey. See FC106 AMR presentations for pol curves and catalyst details.

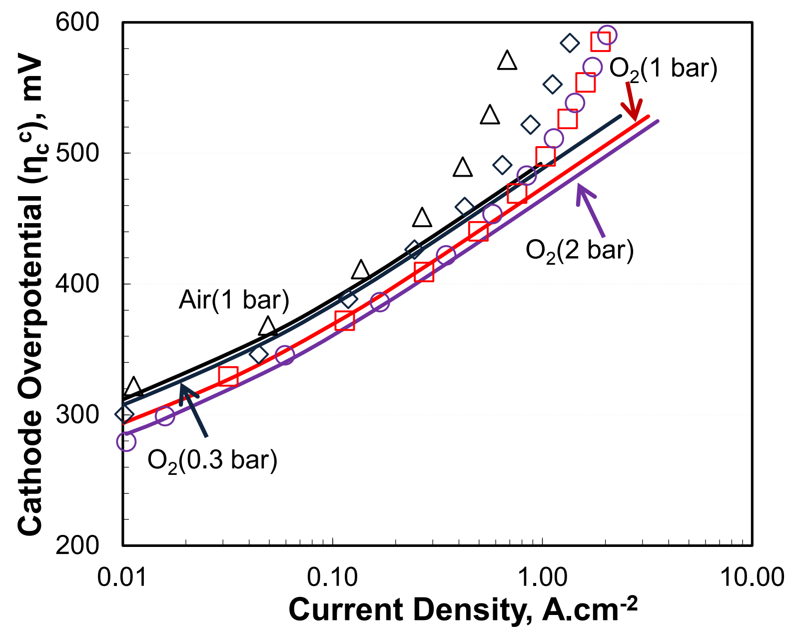
Distributed ORR Kinetics Model

$$\eta_c^c = \eta_c + iR_\Omega^c\left(\frac{i\delta_c}{b\sigma_i}\right)$$

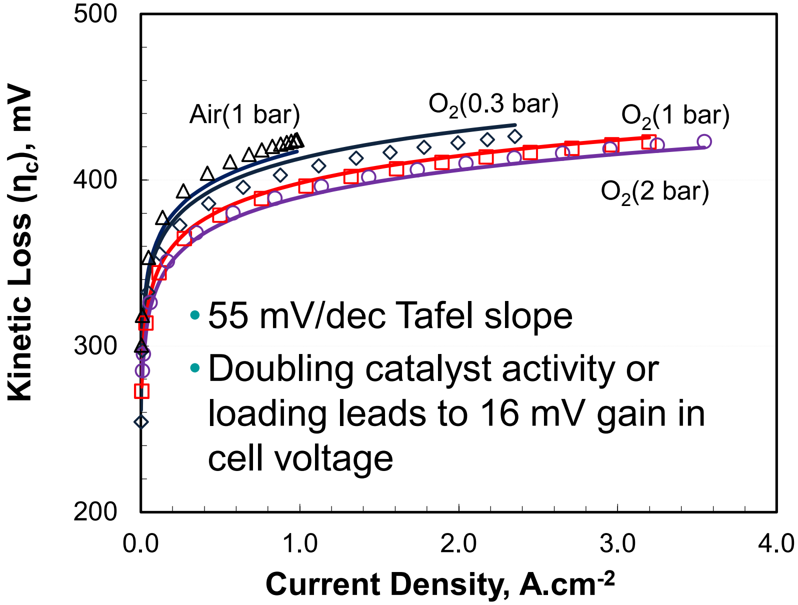
$$i = i_0 P_{O_2}^{\gamma} e^{\frac{\alpha nF}{RT}\eta_c}$$

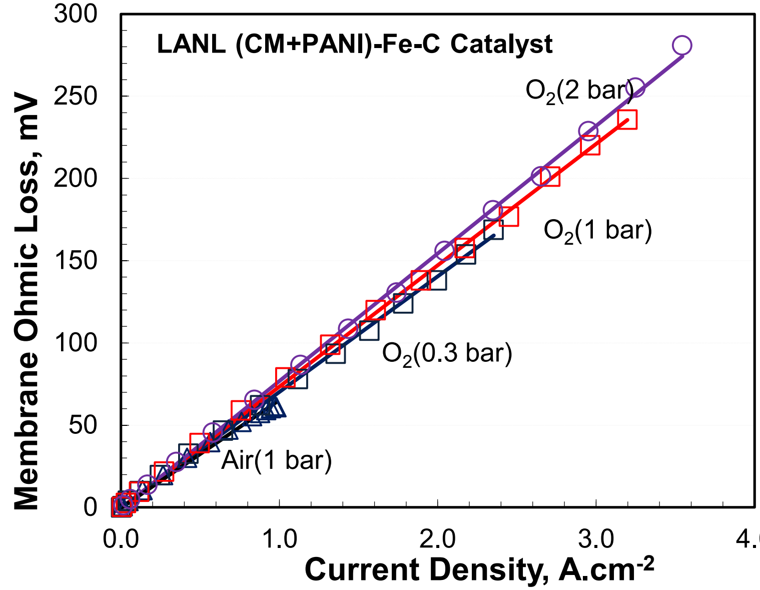
Catalyst	Catalyst Loading	Mass Activity	Catalyst Activity
Pt/C	0.1 mg-Pt/cm^2	443 A/g-Pt	44.3 mA/cm^2
a-Pt/C	0.1 mg-Pt/cm^2	316 A/g-Pt	31.6 mA/cm^2
d-PtNi/C	0.1 mg-Pt/cm^2	665 A/g-Pt	66.5 mA/cm^2
(CM-PANI)-Fe-C	4 mg-cat/cm^2	1.8 A/g-cat	7.2 mA/cm^2

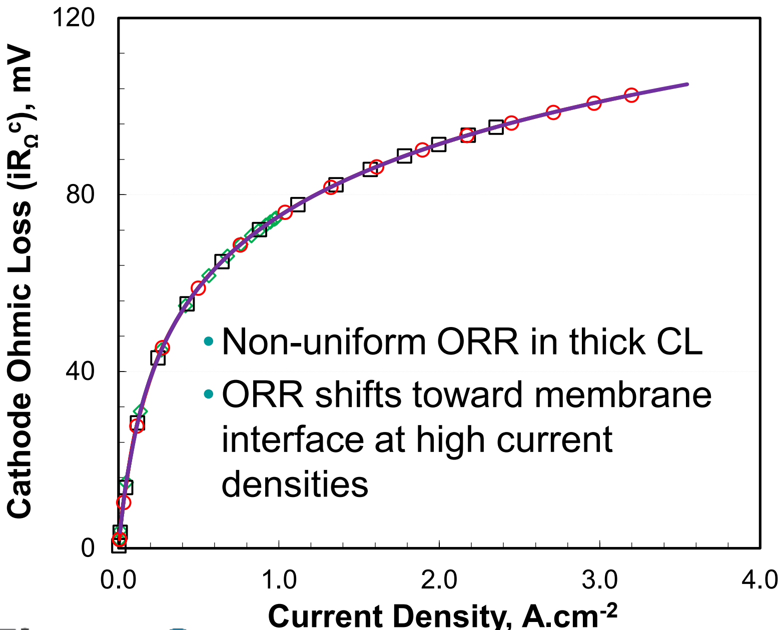


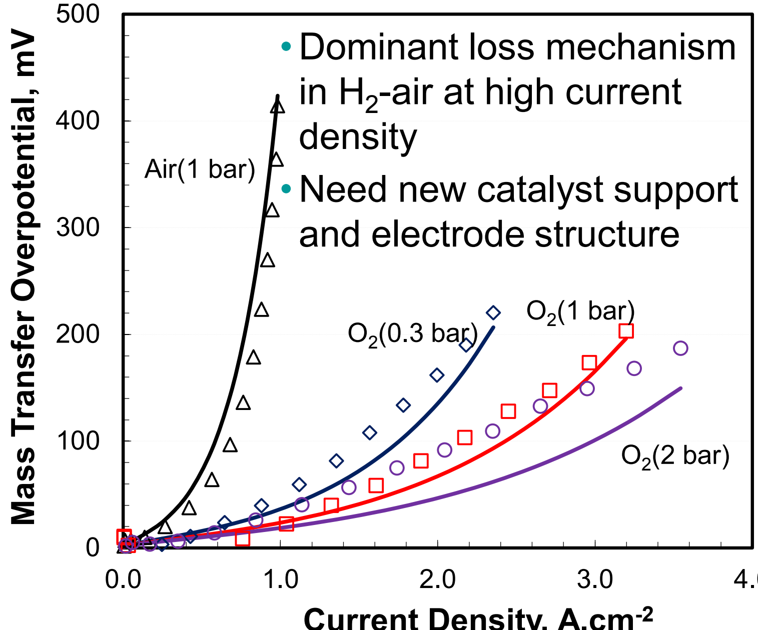


Breakdown of Voltage Losses (80 °C, 100% RH)



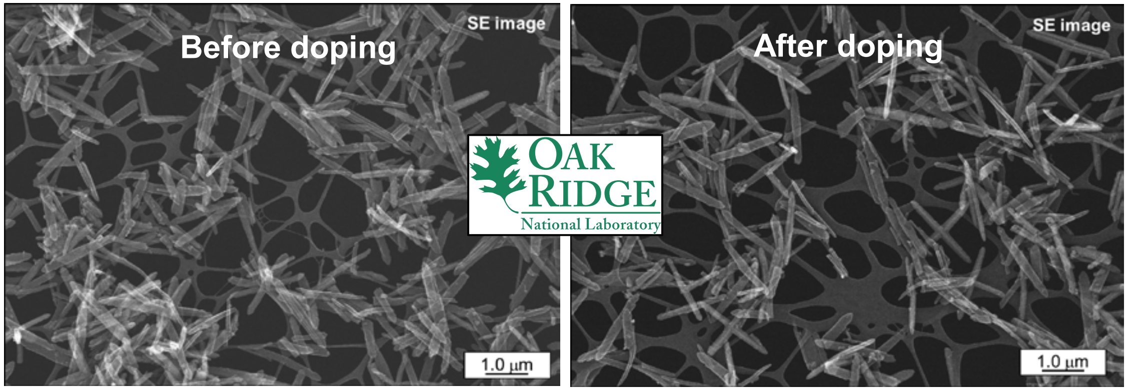


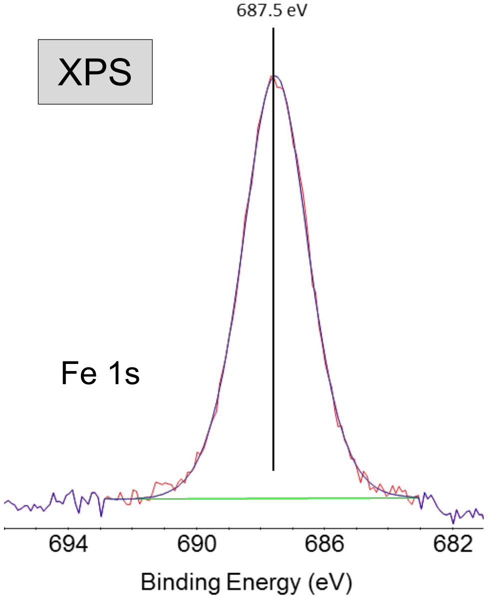


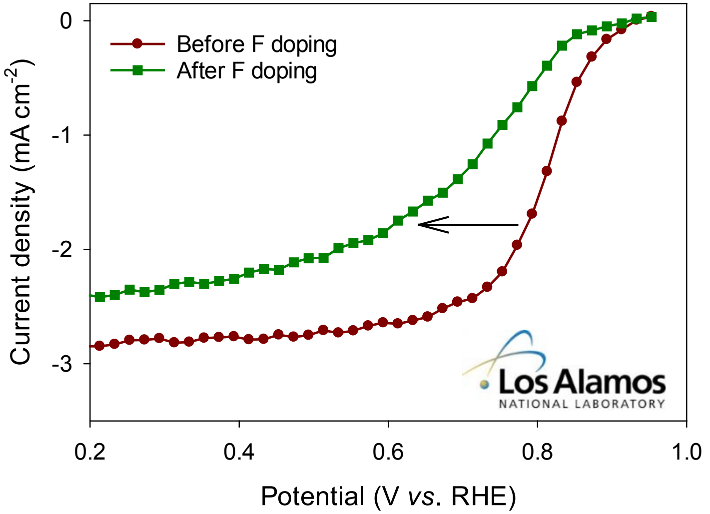


Capability Development: Fluorine Doping of (AD)Fe-N-C Catalyst

Purpose: Prevent flooding of thick PGM-free electrodes by imparting hydrophobicity to catalyst with fluorine doping







	C	O	N	Fe	F	Zn	Al
Before doping	89.0	6.1	3.7	0.9	0.0	0.2	0.0
After doping	78.7	9.2	2.8	**0.3**	**5.8**	0.2	3.0

- No morphological change after fluorine doping
- F successfully doped (5.8 at.%), either within C network or bridge-bonded with two carbons; however, Fe content decreased from 0.9 to 0.3 at.% causing decrease in ORR activity